Studies of the Reactivity of Permethylzirconocene Complexes with Binuclear Transition Metal Carbonyl Compounds

Thesis by

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To My Parents

ACKNOWLEDGMENTS

My stay at Caltech has been immeasurably enriched, both intellectually and personally, by the people I've come to call my friends. The Bercaw group members, past and present, have provided a rowdy, enjoyable atmosphere over the years for which I am grateful. From my introduction to vacuum line technique at the hands of Pete, Rich and Jimmy, to John's attempts to weed out the group in the Sierras, there are countless experiences I would not have had elsewhere. Each group member (including the one that use to hang from the ceiling) has added his or her own particular touch to the office spirit. I am especially grateful to Dean, Nancy, Allan, Francis, Maureen and Martha for their friendship. Of course the 3 R's certainly have made things exciting in lab. I feel very lucky to have spent my graduate career with John Bercaw, whose enthusiasm and remarkable insight into science have never ceased to amaze me. Finally, I thank Suma for making life so pleasant and for helping me keep my perspective on those things which are truly important.

ABSTRACT

The low valent permethylzirconocene complex $\{Cp^*_2ZrN_2\}_2N_2$ ($Cp^* \equiv \eta^5$-C_5Me_5) reacts with binuclear transition metal carbonyl compounds of the general formula $Cp_2M_2(CO)_x$ ($Cp \equiv \eta^5$-C_5H_5) to produce trinuclear complexes. Two major modes of reactivity are observed. Compounds with M-M bonds that are easily reduced such as $[CpM(CO)_3]_2$ (M = W, Mo) react with $\{Cp^*_2ZrN_2\}_2N_2$ to produce trinuclear species in which two $CpM(CO)_3$ anions are connected to a Cp^*_2Zr dication via μ_2-(C-η^1; O-η^1) carbonyl bridges. The structure of the molybdenum complex has been determined by single crystal X-ray diffraction methods. These trinuclear complexes are also produced in the reaction of the Cp^*_2ZrRR' (R,R' = H, alkyl) with two equivalents of the hydride complexes $CpM(CO)_3H$. The dinuclear complexes $Cp^*_2M(H)[CpMo(CO)_3]$ (M = Zr, L = PMe_3; M = Hf, L = CO) have been similarly prepared by treatment of the zirconium or hafnium dihydride with the corresponding molybdenum hydride. The trinuclear complexes react with HX (X = Cl, OH) to produce $CpM(CO)_3H$ and $Cp^*_2ZrX_2$.

The other mode of reactivity between $\{Cp^*_2ZrN_2\}_2N_2$ and metal dimers is observed with $[CpM(CO)_2]_2$ (M = Fe, Ru). In these cases trinuclear complexes are produced in which two carbonyl ligands are reductively coupled yielding an O_2C_2 moiety bridging the three metals. This coupling is reversible and the Zr(II) intermediate can be trapped with CO or other metal dimers. The iron analog is also produced in the reaction of $Cp^*_2ZrI_2$ with $Na[CpFe(CO)_2]$.

The reaction of $\{Cp^*_2ZrN_2\}_2N_2$ with the bridging methylene complex cis-$Cp_2Ru_2(CO)_3(CH_2)$ does not result in carbonyl coupling, yielding instead what appears on the basis of spectroscopic data to be a π-complex between permethylzirconocene and cis-$Cp_2Ru_2(CO)_3(CH_2)$ held together only by μ_2-(C-η^1; C,O-η^2) bridging carbonyl ligands.

The ruthenium carbonyl coupled product, $Cp^*_2Zr(O_2C_2)Ru_2Cp_2(CO)_2$, reacts under H_2 to produce the bridging zirconoxy carbene complex trans-$Cp_2Ru_2(CO)_3(C(H)OZr(H)Cp^*_2)$. This complex is fluxional on the ^1H and ^{13}C NMR timescales. $\Delta G^{\ddagger}$ for this process is 14.0(2) kcal·mol^{-1} at -4°C. The fluxionality is best explained by a process involving a terminal carbene intermediate. The carbene formation is reversible, and treatment with D_2 results in label incorporation in both the hydride and carbene hydrogen positions. Reaction with CO produces $Cp^*_2Zr(CO)_2$, $(CpRu(CO)_2)_2$ and presumably H_2. Treatment with BF_3 or HBF_4 results in C-O scission and produces the bridging methylene complex $Cp_2Ru_2(CO)_3(CH_2)$. Labeling studies indicate both methylene hydrogens originate on zirconium. This bridging methylene complex can be synthesized in 60% yield by treatment of $(CpRu(CO)_2)_2$ with $LiBEt_3H$ in toluene.

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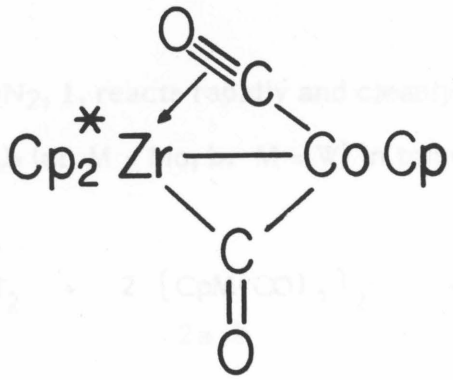
CHAPTER I

Complexes of Permethylzirconocene With Group VI Cyclopentadienyl Anions. Reduction of a Metal-Metal Bond and Formation of μ_2-(C-η^1; O-η^1) Carbonyl Bridges

Introduction

Despite active efforts by several research groups, unequivocal examples of complexes with early/late transiton metal M-M bonds remain relatively uncommon[1,2] compared with the occurrence of M-M bonds between late metal pairs. The comparison is even more stark when only Group IV/late metal pairs are considered.[2] One such complex, $Cp^*_2Zr(CO)_2CoCp$ ($Cp^* \equiv \eta^5$-$C_5(CH_3)_5$), in which the Zr-Co bond is supported by two carbonyl bridges, was characterized in these laboratories.[2a] Thus, we were particularly



interested in preliminary reports that the complexes $Cp_2Zr(CH_3)(CpMo(CO)_3)$[3a] and $Cp_2Zr(C(O)CH_3)(CpMo(CO)_3)$[2b] contained analogous structures. These compounds were prepared with the elimination of methane from Cp_2ZrMe_2 or $Cp_2Zr(CH_3)(C(O)CH_3)$ and $CpMo(CO)_3H$. We have found that a related complex, $Cp^*_2Zr(CpMo(CO)_3)_2$, can be prepared by elmination of H_2 and alkane from $Cp^*_2Zr(H)(R)$ (R = H, alkyl) and two equivalents of $CpMo(CO)_3H$. Subsequent structural characterization of $Cp_2Zr(C(O)CH_3)(CpMo(CO)_3)$ has shown that there is no Zr-Mo bond, and that the metals are connected by a μ_2-(C-η^1; O-η^1) carbonyl or "isocarbonyl" bridge.[4] This type of

interaction is prevalent in complexes between early transition metals and carbonyl compounds.[3] The structure of the dimolybdenum carbonylate species reported in this chapter also exhibits this bonding mode.

It was the trinuclear aspect of $Cp^*_2Zr(CpMo(CO)_3)_2$, however, that presented us with additional questions. In an effort to understand how permethylzirconocene interacts with complexes containing metal-metal bonds we undertook the studies described in this and subsequent chapters.

Results

$\{Cp^*_2ZrN_2\}_2N_2$, **1**, reacts rapidly and cleanly with two equivalents of $(CpM(CO)_3)_2$, **2a,b** (**a:** M = Mo, **b:** M = W) in toluene at 25°C to yield

$$\underset{\mathbf{1}}{\{Cp^*_2ZrN_2\}_2N_2} + 2\ \underset{\mathbf{2a,b}}{(CpM(CO)_3)_2} \longrightarrow$$

$$\underset{\mathbf{3a,b}}{Cp^*_2Zr(CpMo(CO)_3)_2} + 3\ N_2 \qquad (1)$$

red-brown crystals of $Cp^*_2Zr(CpM(CO)_3)_2$, **3a,b.** The ^1H NMR spectrum of **3a** exhibits singlets in the Cp and Cp* regions, while the ^{13}C NMR spectrum shows two signals for carbonyls at 231 and 242 ppm in a 2:1 ratio. Five bands are observed for C-O stretches in the infrared spectrum: 2025, 1945, 1860, 1578 and 1533 cm^{-1}. The latter two, extremely low energy bands are due to the μ_2-(C-η^1; O-η^1) bridging carbonyls.

Compound **3a** is unreactive towards both CO and H_2 at 4 atm and 80°C. Reaction with HX (X = Cl and OH) in benzene at 25°C rapidly yields $Cp^*_2ZrX_2$ and two equivalents of $CpMo(CO)_3H$, **6**. Over days at 80°C, reaction with CH_3I in benzene leads to primarily $Cp^*_2ZrI_2$ and $CpMo(CO)_3Me$.

In addition to direct metal-metal bond reduction, several other routes lead to **3**. At 80°C in benzene, $Cp^*_2Zr(CO)_2$ reacts

$$Cp^*_2Zr(CO)_2 + \underset{\mathbf{4}}{(CpMo(CO)_2)_2} \xrightarrow[\text{benzene}]{80\,^\circ C} \underset{\mathbf{3a}}{Cp^*_2Zr(CpMo(CO)_3)_2} \qquad (2)$$

with $(CpMo(CO)_2)_2$ (M≡M), **4**, to quantitatively yield **3a**. Reaction of **1** with **4** gives purple black solutions of a compound with the probable composition $Cp^*_2Zr(CpMo(CO)_2)_2$, **5**, based on the single Cp and Cp* resonances in a 1:3 ratio observed in the ^1H NMR spectrum. Compound **5** decomposes upon standing in solution to black insoluble material, and has thus far eluded all attempts at isolation. Compound **5** generated <u>in situ</u> reacts with CO to yield primarily **3a**.

Dinuclear elimination of isobutane and hydrogen from $Cp^*_2Zr(H)(CH_2CHMe_2)$ and two equivalents of **6** also produces **3a**. In the reaction of the labeled compound $Cp^*_2Zr(D)(CH_2CDMe_2)$ with **6** (eq. 3), >95% of the hydrocarbon formed is mono-deuterated as determined by ^1H NMR and GC-

$$Cp^*_2Zr(D)(CH_2CDMe_2) \quad + \quad 2\ CpMo(CO)_3H \qquad (3)$$

6

$$\longrightarrow \quad Cp^*_2Zr(CpMo(CO)_3)_2 \quad + \quad HD \quad + \quad (CH_3)_3CD$$

3a

MS analysis. This rules out intramolecular reductive elimination followed by reaction of **6** with permethylzirconocene. Reaction of one equivalent of **6** with $Cp^*_2HfH_2$ at -78°C yields $Cp^*_2Hf(H)(CpMo(CO)_3)$, **7**. The ^1H NMR spectrum of **7** exhibits single Cp and Cp* resonances in addition to the hydride signal at 12.28 ppm. In the infrared spectrum the terminal CO stretches are found at 1938 and 1850 cm^{-1}, with the bridging CO stretch appearing at 1561 cm^{-1}. In addition, the hafnium hydride stretch is found at 1669 cm^{-1}. Stirring **7** in toluene with 1 atm of D_2 at 25°C for 24 h results in deuteration at the hydride position with concurrent loss of the IR and ^1H NMR signals arising from this proton. ^2H NMR spectra show a single enriched resonance at 12.26 ppm.

An analogous mono-molybdenum carbonylate complex of zirconium, $Cp^*_2Zr(H)(CpMo(CO)_2(PMe_3))$, **8**, is formed by the slow addition of $CpMo(CO)_2(PMe_3)H$ to $Cp^*_2ZrH_2$ at -78°C. In this case competing formation of the dicarbonylate species is a greater problem than in the synthesis of **7**. The lower selectivity found for $Cp^*_2ZrH_2$ versus the hafnium dihydride is in keeping with observations that zirconium hydrides are kinetically more reactive than hafnium hydrides.[5] The spectral properties

Table 1. NMR[a] and IR[b] Data.

Compound	IR	Assignment		Chemical Shift
$Cp^*_2Zr\{CpMo(CO)_3\}_2$	ν(CO): 2025(w), 1945(vs),	^1H NMR	$C_5(CH_3)_5$	1.75 (s, 30H)
3a	1860(vs), 1578(vs), 1533(vs)		C_5H_5	5.29 (s, 10H)
		$^{13}C\{^1H\}$NMR	$C_5(CH_3)_5$	11
			C_5H_5	90
			Mo-CO	231
			Mo-COZr	242
$Cp^*_2Zr\{CpW(CO)_3\}_2$	ν(CO): 2022(w), 1940(vs),	^1H NMR	$C_5(CH_3)_5$	1.83 (s, 30H)
3b	1852(vs), 1588(vs), 1542(vs)		C_5H_5	5.22 (s, 10H)
$Cp^*_2Hf(H)\{CpMo(CO)_3\}$	ν(CO): 1938(s), 1849(s), 1542(s)	^1H NMR	$C_5(CH_3)_5$	1.88 (s, 30H)
7	ν(Hf-H): 1668(m)		C_5H_5	5.23 (s, 5H)
			Hf-H	12.28 (s, 1H)

Table 1. Continued.

Compound	IR	Assignment		Chemical Shift
$Cp^*_2Zr(H)(CpMo(CO)_2(PMe_3))$		^1H NMR	$P(C\underline{H}_3)_3$	1.28 (d, 9H, J_{P-H} = 7.5 Hz)
8	ν(CO): 1856(s), 1477(s)		$C_5(C\underline{H}_3)_5$	1.95 (s, 30H)
			$C_5\underline{H}_5$	5.22 (s, 5H)
			Zr-$\underline{H}$	6.45 (s, 1H)

[a]NMR spectra in benzene-d_6 at ambient temperature. Chemical shifts reported in δ relative to internal TMS.
[b]IR spectra obtained as nujol mulls. Values reported in cm^{-1}.

Table 2.

$Cp^*_2Zr(CpMo(CO)_3)_2$

Formula weight = 851.72

monoclinic space group C2/c

MoKα 0.71069 Å

T = 25°C

$1.0 \leq 2\theta \leq 55.0°$

a = 20.009(9) Å

b = 12.145(4) Å

c = 14.595(5) Å

β = 105.18(3)°

Cell volume = 3423(2) $Å^3$

Z = 4

ρ_{calc} = 1.65 g/cc

μ = 25.3 cm^{-1}

R = 0.095 (full data set, N_o = 3523 reflections)

R = 0.053 ($F_o^2 \geq 3\sigma(F_o^2)$ only, N_o = 2113 reflections)

Goodness of fit* = 1.34

Np = 298

*GOF = $[\Sigma w(F_o^2 - s^2F_o^2)^2/(N_o - Np)]^{1/2}$

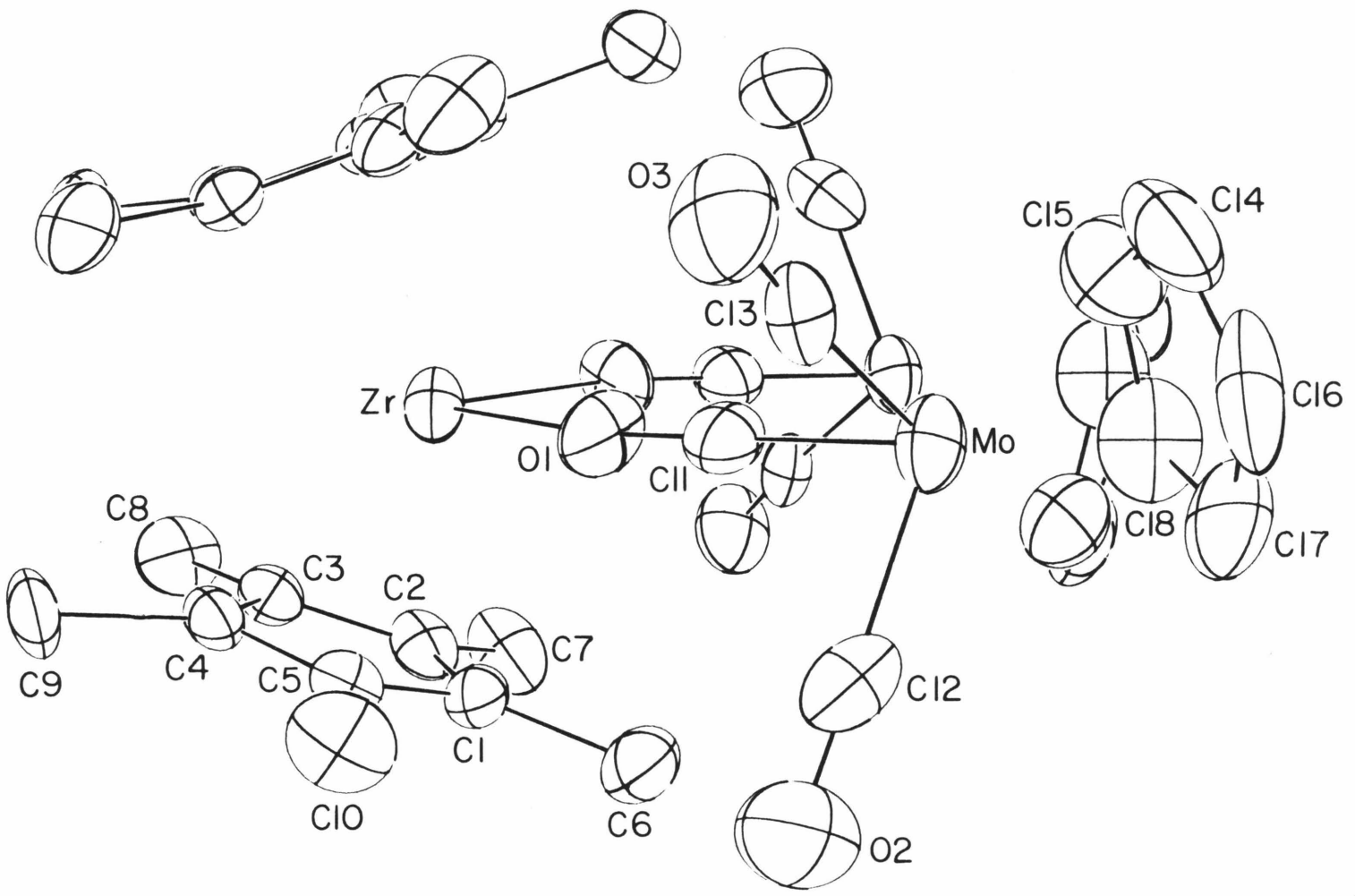


Figure 1. Molecular Configuratioln of $Cp^*_2Zr[CpMo(CO)_3]_2$, **3a.**

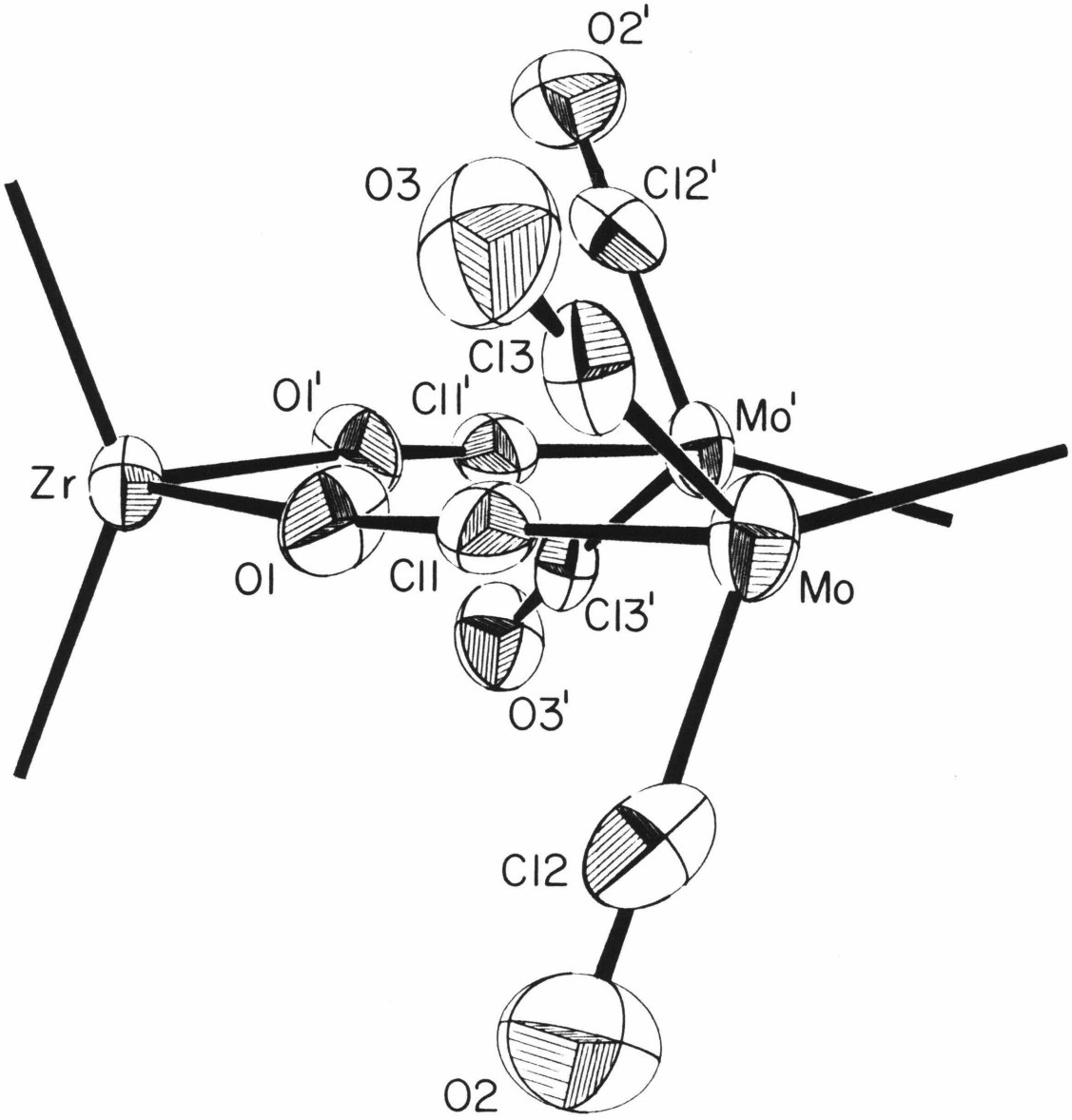


Figure 2. Skeletal view of $Cp^*_2Zr[CpMo(CO)_3]_2$, **3a.**

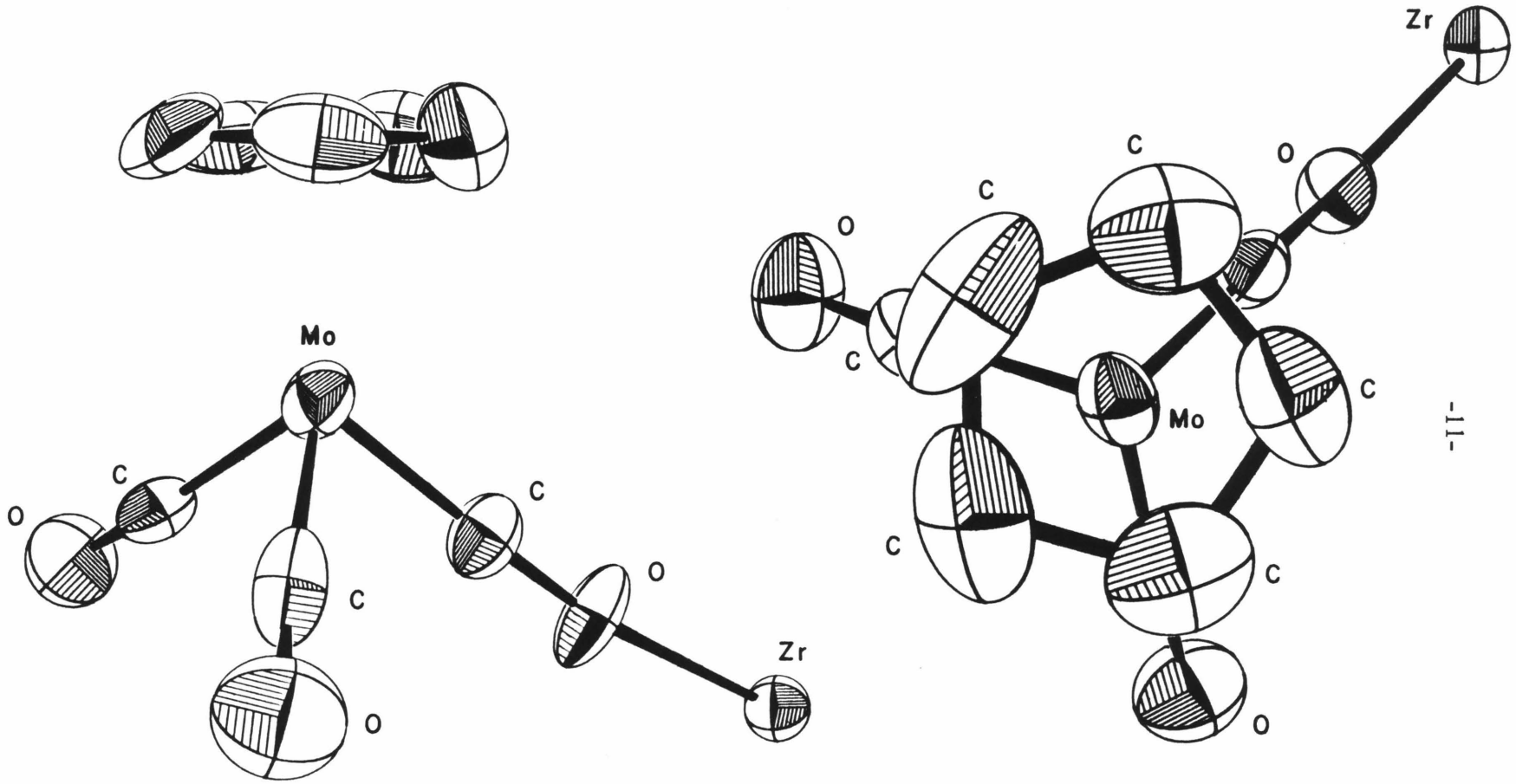


Figure 3. Views of $CpMo(CO)_2(\mu\text{-}CO)Zr$ units in $Cp^*_2Zr[CpMo(CO)_3]_2$, **3a.**

Table 3. Bond distances for $Cp^*_2Zr(CpMo(CO)_3)_2$, **3a** (Å).

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Zr1	O1	2.078 (5)	C3	C2	1.394 (10)
Zr1	C1	2.532 (7)	C3	C4	1.406 (9)
Zr1	C2	2.485 (7)	C4	C5	1.402 (9)
Zr1	C3	2.479 (7)	C5	C1	1.421 (9)
Zr1	C4	2.528 (7)	C5	C10	1.501 (10)
Zr1	C5	2.534 (7)	C7	C2	1.500 (11)
Mo1	C11	1.868 (7)	C8	C3	1.501 (10)
Mo1	C12	1.927 (8)	C11	O1	1.217 (9)
Mo1	C13	1.958 (8)	C9	C4	1.503 (10)
Mo1	C14	2.346 (14)	C14	C15	1.359 (18)
Mo1	C15	2.354 (12)	C14	C16	1.379 (19)
Mo1	C16	2.380 (13)	C15	C18	1.383 (16)
Mo1	C17	2.359 (12)	C16	C17	1.384 (17)
Mo1	C18	2.354 (11)	C17	C18	1.358 (16)
C1	C6	1.507 (10)	O2	C12	1.167 (10)
C2	C1	1.408 (9)	O3	C18	1.133 (10)

Table 4. Bond Angles for $Cp^*_2Zr(CpMo(CO)_3)_2$, **3a** (deg).

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
O1	Zr1	O1'	90.7 (2)	C4	C3	C8	125.8 (6)
C12	Mo1	C11	86.9 (3)	C3	C4	C9	127.1 (6)
C13	Mo1	C11	89.9 (3)	C5	C4	C3	108.5 (6)
C13	Mo1	C12	91.3 (3)	C5	C4	C9	124.3 (6)
C11	O1	Zr1	170.7 (5)	C1	C5	C4	107.7 (6)
C5	C1	C2	107.1 (6)	C1	C5	C10	126.7 (6)
C6	C1	C2	125.3 (6)	C10	C5	C4	124.7 (6)
C6	C1	C5	126.3 (6)	O1	C11	Mo1	177.8 (6)
C1	C2	C3	109.0 (6)	C16	C14	C15	109.4 (12)
C1	C2	C7	125.2 (6)	C18	C15	C14	106.8 (11)
C7	C2	C3	125.7 (6)	C17	C16	C14	106.8 (11)
C2	C3	C4	107.7 (6)	C18	C17	C16	107.9 (11)
C2	C3	C8	126.4 (6)	C17	C18	C15	109.1 (10)

of **8** are similar to those of **7**. NMR and IR data are presented in Table 1.

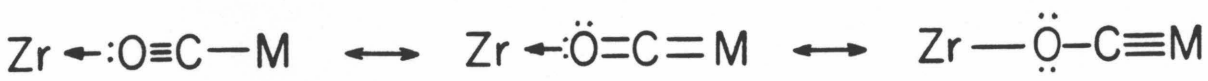
The structure of **3a** was confirmed by single crystal X-ray diffraction analysis.[6] Crystal data and details of the structure determination are given in Table 2. The structure of **3a** is shown in Figures 1 and 2. The molybdenum units are very regular "three-legged piano stools" as shown in Figure 3. The molybdenum and zirconium atoms are connected via μ_2-(C-η^1; O-η^1) carbonyl, or "isocarbonyl" linkages. The ($CpMo(CO)_3$) units and Cp* rings are related by a two-fold crystallographic axis containing the zirconium atom, with one molybdenum slightly above the equatorial plane of the Cp^*_2Zr unit, and one slightly below. At 170.7(5)°, the Zr-O-C angles are nearly linear, as are the Mo-C-O angles. Complete lists of bond angles and distances are found in Tables 3 and 4.

Discussion

Of the great number of organometallic compounds containing more than a single transition metal, a very large proportion contain coordinated carbon monoxide. In a large number of these complexes carbon monoxide bridges two or more metals in one of several modes.[7] While the most common binuclear bridging mode, μ_2-η^2, has been recognized since the structure determination of $Fe_2(CO)_9$ in 1939,[8] it has been only within the last decade that other possibilities have been observed. This is no doubt partially due to the advances in crystallography as well as the tremendous number of new compounds synthesized since the explosion of interest in organo-transition metal chemistry.

The four primary binuclear bridging modes for CO are shown in Figure 4. The first three modes, μ_2-η^2, semi-bridging and μ_2-(C-η^1; C,O-η^2) are always found bridging two metals that are directly bonded. The μ_2-(O-η^1; C-η^1) bonding mode, however, always bridges two metals that are not otherwise connected. Several examples of this mode have been reported.[3] As might be expected, the different ends of carbon monoxide show different preferences for metal center types. The carbon-donor end binds to low valent, electron-rich metals in much the same manner as do terminal carbonyls. The oxygen-donor end, by contrast, is more basic and inevitably binds to Lewis acidic centers. In fact, this bonding mode is commonly found between transition metal carbonyl anions and Lewis acidic main group cations such as Al(III),[9] Mg(II),[10] and Na(I).[11]

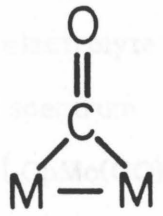
The major resonance structures for the μ_2-(C-η^1; O-η^1) carbonyl bridges in **3** are shown below. **A** involves a dative interaction



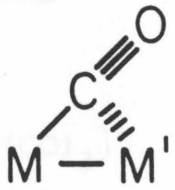
A **B** **C**

between an anionic metal carbonyl complex and a cationic zirconium center. In **B** the dative interaction still persists, but there is some π-backbonding. **C** represents the structure with complete π-backbonding from the metal to the bridging ligand.

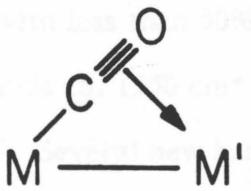
I symmetrical bridge



II "semibridging"



III $\mu_2-\eta^1,\eta^2$ bridging



IV $\mu_2-\eta^1,\eta^1$ bridging

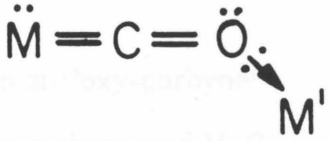


Figure 4. Principal binuclear bridging modes of the carbonyl ligand.

Based on resonance structures **A** and **B**, one might expect that the metal centers could be solvated in coordinating media. Norton et al. reported that $Cp_2Zr(C(O)Me)(CpMo(CO)_3)$ appears to be a 1:1 electrolyte in acetonitrile.[4] In addition, they report that the infrared spectrum of this compound in acetonitrile is consistent with free $(CpMo(CO)_3)^-$ anion (eq. 4). A similar result has been reported in the case of

$$Cp_2Zr(C(O)Me)(CpMo(CO)_3)^- \xrightarrow{CH_3CN} Cp_2Zr(C(O)Me)(CH_3CN)^+ + (CpMo(CO)_3)^- \qquad (4)$$

$Cp^*_2Ti(CpMo(CO)_3)_2$ in DME.[12] Compounds **3a** and **3b** are not stable in DME or acetonitrile, but the solution infrared spectra taken with less than 50% decomposition show the absence of the pair of strong bands ca. 1550 cm^{-1}, and the appearance of a single, weak band at 1590 cm^{-1}. Several new bands are found between 2000 and 1700 cm^{-1}. This is consistent with dissociation of at least one $CpM(CO)_3$ anion, although $Cp^*_2Zr^{n+}$ (n = 1 or 2) appears to be a strong enough Lewis acid to undergo subsequent further reactions with DME.

In **C** on the other hand, the backbonding results in an "oxy-carbyne" structure with no formal charge separation. This implies a shortened M-C distance and a lengthened C-O distance. In **3a**, the latter distance is clearly longer than in the terminal carbonyl ligands (1.217(9) vs 1.150(11) Å (average)), but this is still ca. 0.2 Å shorter than a typical C-O single bond.[13] Stuckey has reported the structure of a cationic titanium-DME

complex, $(Cp_2TiDME)_2^+(Zn_2Cl_6)^{2-}$, in which the C-O single bond in the bound DME is 1.305(8) Å.[14] The Mo-C distance is significantly shorter than in the terminal carbonyls [1.868(7) vs 1.942(8) Å (average)]. There are data available for only one molybdenum carbyne, $Re(CO)_9Mo(CPh)$.[15] At 1.835(25) Å the M-C triple bond is slightly longer than the 1.829 Å calculated from average Mo-Mo and C-C triple bonds.[15] Reported W-C triple bond distances vary over the range 1.775 to 1.842 Å, or at least 0.1 Å shorter than typical W-C and Mo-C distances in carbonyls.[16] These comparisons do not unambiguously demonstrate participation of structure **C** in the bonding picture of **3a**, but the trends in bond length are in the correct direction.

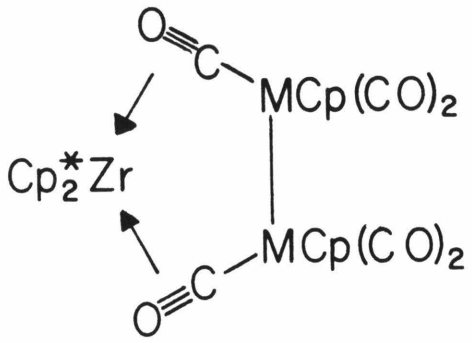
Recently Casey and coworkers reported a new structural pattern for compounds containing both zirconium and a second transition metal.[2c] The complexes $Cp_2Zr(R)(CpM(CO)_2)$ (R = Cl, Me, O-t-Bu; M = Fe, Ru) represent rare examples of unbridged early/late transition metal M-M bonds. The electron density on the metals in the $CpM(CO)_2$ anions is considerably higher than on the molybdenum in $CpMo(CO)_3^-$ which has one additional carbonyl and two fewer d-electrons. The iron and ruthenium anions are also much less sterically encumbered. Both factors clearly favor direct metal-zirconium interactions. The absence of low energy bands in the IR make assignment of this unbridged structure relatively simple.

The problem arises in structures containing bonds between zirconium and a metal with type III bridging carbonyls. Distinguishing between type III and type IV bridging carbonyls on the basis of C-O stretching frequencies is not a straightforward matter. Type IV μ-CO stretches have been reported

between 1690 and 1533 cm^{-1}.[3] By comparison, type III μ-CO stretches range from 1683 to 1560 cm^{-1}.[1,2] Our original intention in synthesizing **8** was to increase electron density of the molybdenum sufficiently to disfavor a type IV bridge and favor a Mo-Zr bond. The infrared spectrum of **8** shows bands at 1843 and 1477 cm^{-1}. While the structural assignment is open to debate, we believe that the low energy band at 1477 cm^{-1} is due to a type IV bridge, analogous to **3a**. It is likely that the combination of Cp* rings and the large anion precludes the close approach of the directly bonded structure on steric grounds. In keeping with the increased electron density in the phosphine substituted case, the CO stretching frequencies in **8** are all shifted to lower energy. That the bridging CO band shifts to a greater extent is to be expected, as the zirconium should increase the π-acceptor properties of this ligand as suggested by resonance structure **C**.

The formation of **3**, **7**, and **8** by dinuclear elimination is well precedented.[2b,3a] It has quite reasonably been suggested that later metal hydrides react with zirconium alkyls <u>via</u> a proton transfer mechanism.[4] The reduction of the metal-metal bond in **2** by **1** bears further comment. Using the bonding description **A**, the net result of the reaction of **1** with **2** is oxidation of zirconium from the divalent to the tetravalent state with concomitant reduction of the M-M bond yielding two $CpM(CO)_3$ anions. This is comparable to the two electron reduction of **2a,b** with Mg/Hg.[10] In addition, recent reports describe Cp^*_2Yb[3f] and $Cp_2Ti(CO)_2$[3a] as one electron reductants with $Co_2(CO)_8$ and **4**. The reduction of **2** may be envisioned as proceeding <u>via</u> outer sphere electron transfer to **2** from **1** prior to dissociation of the dinitrogen ligands, or alternatively, by coordination of the molybdenum

dimer to permethylzirconocene followed by inner sphere electron transfer. The inner sphere process could proceed via loss of the N_2 ligands in **1**, followed by formation of the transient zirconium(II) complex **D**. Electron



D

transfer would then yield **3**. Type III (π-bound) carbonyl bridges are fairly common among early transition metal complexes, although a structure held together only by such linkages has no precedent.[17]

Outer sphere reduction of **2** by divalent zirconium is indicated in the formation of **3a** in a different system. Recent studies of the carbonyl coupled compound $Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2$, **9**, have shown that this complex undergoes several substitution reactions through a Zr(II) intermediate.[18] While the exchange of $[Cp'Fe(CO)_2]_2$ ($Cp'\equiv C_5H_4Me$) for $[CpFe(CO)_2]_2$ in **9** takes >one week at 25°C (eq. 5), **9** reacts with **2a** to produce **3a** and

$$\underset{\mathbf{9}}{Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2} + [Cp'Fe(CO)_2]_2$$

$$\xrightleftharpoons{>1\ \text{week}} \underset{\mathbf{9}}{Cp^*_2Zr(O_2C_2)Fe_2Cp'_2(CO)_2} + [CpFe(CO)_2]_2 \qquad (5)$$

$$\underset{\mathbf{9}}{Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2} + \underset{\mathbf{2a}}{(CpMo(CO)_3)_2}$$

$$\xrightarrow[\text{benzene}]{\text{seconds}} (CpFe(CO)_2)_2 + \underset{\mathbf{3a}}{Cp^*_2Zr(CpMo(CO)_3)_2} \quad (6)$$

$(CpFe(CO)_2)_2$ within seconds (eq. 6). This has been explained in terms of an outer sphere electron transfer process, i.e., without coordination of **2a**.[18] In lieu of some method for distinguishing between inner and outer sphere processes in the reaction of **1** with **2**, both mechanisms must be considered viable.

Merola has proposed that the reaction has proposed that the reaction of $Cp^*_2Zr(CO)_2$ with the unsaturated dimer **4** proceeds via initial CO transfer to yield **2a** and titanocene, "Cp_2Ti", which subsequently form the observed product, $(Cp_2Ti(CpMo(CO)_3))_2$.[3e] Our findings are in accord with this proposal. $Cp^*_2Zr(CO)_2$ reacts with **4** to produce **3a** (eq. 2) but under much more forcing conditions than required by reaction of **1** with **2a**.

Experimental Section

General Considerations. All of the manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$, then from "titanocene," prepared as described earlier.[19] Benzene-$\underline{d}_6$ and toluene-$\underline{d}_8$ (Stohler, Inc.) were vacuum transferred from "titanocene." Hydrogen and deuterium (Matheson) were purified by passage over activated 4 Å molecular sieves and MnO on vermiculite.[20] Carbon monoxide and hydrogen chloride (MCB) were used directly from the cylinder.

^1H NMR spectra were recorded on Varian EM-390 and JEOL FX-90Q spectrometers. The latter machine was used to measure ^{13}C spectra. Infrared spectra were measured on a Beckman IR-4240 spectrophotometer. $\{Cp^*_2ZrN_2\}_2N_2$,[21] $Cp^*_2ZrH_2$,[22] $Cp^*_2Zr(D)(iso\text{-}C_4H_8D)$,[22] $Cp^*_2Zr(CO)_2$,[23] $Cp^*_2Zr(CH_3)_2$,[22] $Cp^*_2HfH_2$,[5] $[CpMo(CO)_3]_2$,[24] $[CpMo(CO)_2]_2$,[25] and $CpMo(CO)_3H$[26] were prepared as described previously.

Elemental analyses were performed by Bernhardt Microanalytical Laboratory, Dornis and Kolbe Microanalytical Laboratory, or by Larry Henling at the CIT analytical service.

Several reactions were carried out in sealed NMR tubes and monitored by NMR spectrometry. A typical example is the reaction of $Cp^*_2Zr(CO)_2$ with $[CpMo(CO)_2]_2$: 20 mg (0.048 mmol) $Cp^*_2Zr(CO)_2$ and 20 mg (0.046 mmol) $[CpMo(CO)_2]_2$ were placed in an NMR tube sealed to a ground glass joint and fitted with a Teflon needle valve adapter. Benzene-$\underline{d}_6$ (ca. 0.3 mL was distilled into the tube at -78°C and the tube was sealed with a torch.

$Cp^*_2Zr(CpMo(CO)_3)_2$, 3a. Onto 300 mg (0.37 mmol) **1** and 365 mg (0.75 mmol) **2a** was distilled 50 mL toluene at -196°C. The mixture was allowed to warm to 25°C with stirring. Within 20 min the solution had gone from deep purple to dark orange-red. After an additional 2 h stirring the solvent was stripped off and the evolved gas was collected and analyzed via Toepler pump. Non-combustible gases totaled 1.06 mmol, or 95% of the expected N_2. The flask containing the residue was attached to a small swivel frit. Recrystallization from toluene yielded 340 mg (54%) of red-brown micro-crystalline solid. A second crop of 120 mg (19%) was obtained in the same manner.

Anal. calcd. for $C_{36}H_{40}Mo_2O_6Zr$: C, 50.76; H, 4.73; Mo, 22.53; O, 11.26; Zr, 10.71. Found: C, 50.52; H, 4.85; Mo, 22.69; Zr, 10.88.

$Cp^*_2Zr(CpW(CO)_3)_2$, 3b. Onto 410 mg (0.51 mmol) **1** and 610 mg (0.92 mmol) **2b** was distilled 30 mL toluene at -196°C. The mixture was allowed to warm to 25°C with stirring. After 1 h the red-brown solid was collected on the frit, washed once with 5 mL toluene and dried in vacuo, yielding 655 mg (70%).

Anal. calcd. for $C_{30}H_{40}O_6W_2Zr$: C, 42.07; H, 3.92; O, 9.34; W, 35.78; Zr, 8.88. Found: C, 42.68; H, 4.07; Zr, 9.38.

$Cp^*_2Hf(H)(CpMo(CO)_3)$, 7. Onto 450 mg (1.00 mmol) $Cp^*_2HfH_2$ and 245 mg (1.00 mmol) **6** was distilled 20 mL toluene at -196°C. The mixture was allowed to warm to -78°C with stirring, at which point the solution began to turn light yellow with gas evolution. After 1 h gas evolution had ceased. The yellow solution was then filtered, and the solvent stripped off to leave a yellow oil. Trituration with 20 mL petroleum ether, followed by filtration

and a single washing with petroleum ether yielded 490 mg (71%) of yellow crystalline solid. A second crop of 90 mg (13%) was obtained in the same manner.

Anal. calcd. for $C_{28}H_{36}HfMoO_3$: C, 48.39; H, 5.22; Hf, 25.68; Mo, 13.81; O, 6.90. Found: C, 48.21; H, 5.10; Hf, 25.91.

$Cp^*_2Zr(H)(CpMo(CO)_2(PMe_3))$, 8. A solution containing 85 mg (0.03 mmol) $CpMo(CO)_2(PMe_3)H$ in 15 mL petroleum ether was added dropwise via syringe to 110 mg (0.03 mmol) $Cp^*_2ZrH_2$ in 15 mL petroleum ether at -78°C. During addition the reaction mixture went from pale yellow to red-orange. The solution was allowed to warm to 25°C, and was filtered. Solvent volume was reduced to 10 mL and cooled slowly to -78°C. Filtration and removal of solvent yielded 105 mg (55%) of yellow solid. ^1H NMR of the filtrate showed a mixture of mono- and di-molybdate species.

Anal. calcd. for $C_{30}H_{45}MoO_2PZr$: C, 54.94; H, 6.92; Mo, 14.63; O, 4.88; P, 4.72; Zr, 13.91. Found: C, 54.87; H, 7.01; P, 4.86; Zr, 14.12.

Exchange of D_2 With $Cp^*_2Hf(H)(CpMo(CO)_3)$, 7. A solution of 50 mg **7** in 25 mL petroleum ether was stirred under 1 atm D_2 for 24 h at 25°C. The solvent was stripped off, and 45 mg yellow solid scraped from the flask. ^1H NMR showed an unchanged spectrum of **7** minus the hydride signal at 12.28 ppm. ^2H NMR showed a single peak at 12.26 ppm.

Reaction of $Cp^*_2Zr(D)(iso\text{-}C_4H_8D)$ With $CpMo(CO)_3H$. $Cp^*_2Zr(D)(iso\text{-}C_4H_8D)$ (35 mg, 0.08 mmol), **6**, (40 mg, 0.16 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Within 1 min of reaching 25°C the mixture was deep red-orange. The ^1H NMR spectrum indicated quantitative conversion to **3a** and $(CH_3)_3CD$ (1:1:1 triplet at 0.85 ppm, J_{H-D} = 1 Hz).

GC-MS of residual gas in NMR tube indicates less than 5% of $(CH_3)_2(CH_2D)CD$ (mass 60).

Reaction of $\{Cp^*_2ZrN_2\}_2N_2$ With $[CpMo(CO)_2]_2$. Compound 1 (20 mg, 0.03 mmol), 4 (22 mg, 0.05 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Within 1 min of reaching 25°C the mixture was black purple. The ^1H NMR spectrum indicated a nearly quantitative reaction with two new singlets at 5.13 and 1.79 ppm in a ratio of 1:3. After one week at 25°C the spectrum showed complete decomposition. Separate attempts to isolate this material at low temperature were not successful.

Reaction of $\{Cp^*_2ZrN_2\}_2N_2$ With (1) $[CpMo(CO)_2]_2$ (2) CO. Onto 1 (20 mg, 0.03 mmol) and 4 (22 mg, 0.05 mmol) was distilled 10 mL of toluene at -78°C. After stirring at 25°C for 10 min the purplish black solution was cooled to -78°C and 400 torr CO introduced into the flask. After stirring at 25°C for 1 h the dirty red-orange solution was stripped of solvent. ^1H NMR of the residue indicated that while the reaction was not quantitative, the majority of the product was **3a**.

Reaction of $Cp^*_2Zr(CO)_2$ with $[CpMo(CO)_2]_2$. $Cp^*_2Zr(CO)_2$ (20 mg, 0.05 mmol), $[CpMo(CO)_2]_2$, (20 mg, 0.05 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube and the reaction was periodically monitored by ^1H NMR spectrometry. Conversion to **3a** was complete after 12 h at 80°C.

Reaction of $Cp^*_2Zr(CH_3)_2$ with $CpMo(CO)_3H$. $Cp^*_2Zr(CH_3)_2$ (32 mg, 0.08 mmol), $CpMo(CO)_3H$ (40 mg, 0.16 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Reaction of initially one, followed by a second equivalent of $CpMo(CO)_3H$ was followed by ^1H NMR spectrometry.

Quantitative conversion to **3a** was complete after ten days at 25°C

Attempted Reaction of 3a with H_2. Compound **3a** (10 mg, 0.01 mmol), H_2 (0.07 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube at -196°C. No reaction was observed by ^1H NMR spectrometry after three months at 80°C.

Attempted Reaction of 3a with CO. Compound **3a** (10 mg,0.01 mmol), CO (0.04 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. No reaction was observed by ^1H NMR spectrometry after one week at 80°C.

Reaction of 3a with HCl. Compound **3a** (10 mg, 0.01 mmol) HCl (38 torr, 19.8 mL at 25°C, 0.04 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Immediately upon warming to 25°C the mixture became light yellow. The ^1H NMR spectrum indicated quantitative conversion to $Cp^*_2ZrCl_2$ and $CpMo(CO)_3H$, by comparison with the known compounds.

Reaction of 3a with H_2O. Compound **3a** (10 mg, 0.01 mmol), H_2O (0.02 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Immediately upon warming to 25°C the mixture was light yellow. The ^1H NMR spectrum indicated quantitative conversion to $CpMo(CO)_3H$ and $Cp^*_2Zr(OH)_2$.

Reaction of 3a with CH_3I. Compound **3a** (10 mg, 0.01 mmol), CH_3I (22 torr, 19.8 mL at 25°C, 0.02 mmol), 0.3 mL of benzene-d_6, and TMS were sealed in an NMR tube. Reaction was complete after three days at 80°C. The ^1H NMR spectrum indicated the major Zr containing product was $Cp^*_2ZrI_2$. Some $CpMo(CO)_3CH_3$ was observed along with an equal amount of $(CpMo(CO)_3)_2$.

Structure Determination of $Cp^*_2Zr(CpMo(CO)_3)_2$. A series of oscillation and Weissenberg photographs (Co Kα) indicated a monoclinic cell with systematic absence hkl, h + k odd and h0l, l odd, consistent with space groups Cc or C2/c. A crystal with dimensions 0.4 x 0.2 x 0.2 mm was mounted in a glass capillary under N_2 with its long axis slightly skewed to the φ-axis of a Syntex $P2_1$ diffractometer. Unit cell dimensions were obtained by a least-squares fit of the $\sin^2\theta/\lambda^2$ values of 15 reflections measured on the diffractometer. The calculated density of 1.65 g/cc (assuming Z = 4) is reasonable for organometallic compounds of this type. Using Mo Kα radiation monochromated with a graphite crystal, one hemisphere of data was measured between 1.0 and 55.0° in 2θ, using a θ-2θ scan technique with a scan range of 1° and a scan rate of 1°/min. Background counts were taken for 15 seconds before and after each scan. Intensities of three check reflections measured every 100 reflections showed a systematic rise of ca. 3%. This was attributed to the X-ray tube current rising from 20.0 to 20.6 mA over the course of 4443 reflections. The intensities were scaled to account for this rise over the collection time. Intensities and their variances were corrected for Lorentz and polarization effects. No absorption correction was applied (μ = 25.3 cm^{-1}). The data set was placed on a absolute scale by means of a Wilson plot using scattering factors for Zr and Mo calculated from Cromer and Mann,[27] and for C,H, and O from Cromer and Waber.[28] The Wilson statistics clearly indicated a centric space group. Thus the correct space group is C2/c, as confirmed by the successful structure solution and refinement. Systematic absences and one reflection having an extremely unsymmetrical background were deleted, leaving 3523 reflections

for the working data set.

Solution and Refinement.[29] The locations of the three metal atoms were determined from a three-dimensional Patterson map. This shows that the molecule sits on a two-fold rotation axis, making only half of the atoms unique. A structure factors computation using these positions gave an R index ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.506. The Fourier map showed the positions of all of the non-hydrogen atoms. Several cycles of least-squares refinement using isotropic Gaussian amplitude parameters led to a R index of 0.165. At this point anisotropic Gaussian amplitudes were introduced. Two cycles of least-squares refinement yielded an R index of 0.106. Since the hydrogen atom positions could not be reliably determined from the difference Fourier map, they were placed at positions calculated using C-H bond lengths of 0.9 Å and tetrahedral and trigonal geometries around Cp* and Cp carbons, respectively. This allowed further refinement of the thermal parameters for these carbon atoms. Two cycles of refinement, leaving the hydrogen positions and their Gaussian amplitudes unrefined, and including the scale factor, gave an R index of 0.095 with a goodness of fit of 1.34. Further least-squares refinements yielded no decrease in the R index. A structure factors calculation using only data with $F_o^2 \geq 3\sigma(F_o^2)$ gave an R index of 0.053 (2113 reflections). Difference Fourier maps generated in the plane of the Cp ring and in the planes perpendicular to the ring carbon-methyl carbon bonds in the Cp* did not help in locating the true positions of the hydrogen atoms. Relevant data concerning the structure are presented in Tables 2-5. Supplementary material including calculated hydrogen atom positions, structure factor amplitudes, positional and thermal parameters is available.

Table 5. Least-Squares Planes

Atom	Deviation From Plane (Å)
Cp*	
C1	0.0078
C2	-0.0119
C3	-0.0006
C4	0.0114
C5	-0.0066
Cp	
C14	-0.0063
C15	0.0019
C16	0.0081
C17	-0.0070
C18	0.0033

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CHAPTER II

Reductive Coupling of Carbonyl Ligands in Binuclear Transition Metal Complexes. Reversible C-C Bond Formation in Reactions of Permethylzirconocene.

Introduction

There has been a great deal of interest recently in complexes containing both early and late transition metals. The relative paucity of such complexes combined with the belief that they might behave quite differently from complexes containing more similar metals has sparked many research efforts in this area. Our original involvement with heteronuclear complexes of zirconium stemmed from studies of the reduction of transition metal-bound carbon monoxide by $Cp^*_2ZrH_2$ ($Cp^* \equiv \eta^5$-$C_5(CH_3)_5$).[1]

The formation of zirconoxy carbene complexes by hydride transfer to terminal carbonyl ligands has been shown to be a fairly general process.[2] However, it was observed that in certain instances hydride transfer did not occur.[3] In these cases reductive elimination was induced and complexes of permethylzirconocene and the transition metal carbonyl compounds resulted. For example, $Cp^*_2ZrH_2$ reacts with $CpCo(CO)_2$ to produce H_2 and $Cp^*_2Zr(CO)_2CoCp$, in which a Zr-Co bond is supported by two different types of bridging carbonyl ligands.[3]

A natural extension of this work was the study of reactive Zr(II) complexes with transition metal dimers. In the initial studies it was found that divalent zirconium in the form of the dinitrogen complex $\{Cp^*_2ZrN_2\}_2N_2$, 1, reduces $(CpMo(CO)_3)_2$ to form $Cp^*_2Zr(CpMo(CO)_3)_2$ with evolution of N_2. This work is described in detail in the preceding chapter.

In our survey of the reactions of 1 with other metal dimers a second, more interesting mode of reactivity was discovered. Iron and ruthenium carbonyl dimers react with 1 to yield trinuclear complexes in which two carbonyl ligands are reductively coupled producing a new carbon-carbon bond

in the form of a O_2C_2 moiety linking the three metals.[4] The carbonyl coupled products are of interest both in terms of conversion of carbon monoxide into a two-carbon fragment and also as a new structural mode for early/late transition metal combination complexes. In this chapter the synthesis, characterization and reactivity of these and related complexes are discussed.

Results

$\{Cp^*_2ZrN_2\}_2N_2$, **1**, reacts with the transition metal carbonyl dimers $[(C_5H_4R)M(CO)_2]_2$ (**2a:** M = Fe, R = H; **2b:** M = Fe, R = Me; **2c:** M = Ru, R = H) in toluene to yield nitrogen and complexes with the stoichiometries $Cp^*_2Zr(O_2C_2)M_2(CO)_2(C_5H_4R)_2$ (**2a:** M = Fe, R = H; **2b:** M = Fe, R = Me; **2c:** M = Ru, R = H). Spectral data for these compounds are listed in table 1. The

$$\underset{\textbf{1}}{1/2\{Cp^*_2ZrN_2\}_2N_2} + \underset{\textbf{2a,b,c}}{[(C_5H_4R)M(CO)_2]_2} \longrightarrow 3/2\ N_2 + \underset{\textbf{3a,b,c}}{Cp^*_2Zr(O_2C_2)[(C_5H_4R)M(CO)]_2} \quad (1)$$

spectral properties of **3a** are representative of the series. The ^1H NMR spectrum of **3a** exhibits two resonances at δ 4.81 (10H) and 1.69 (30H) attributable to Cp and Cp* protons. In the ^{13}C NMR spectrum resonances at δ 268 and 305 are observed in addition to signals for the Cp and Cp* ligands. The infrared spectrum for **3a** exhibits four bands due to ν(CO): 1768(w), 1729(s), 1295(ms), and 1282(ms) cm^{-1} [$\nu(^{13}CO)$: 1730, 1636, and 1260 cm^{-1}

Table 1. NMR[a] and IR[b] Data.

Compound	Infrared ν(CO)	Assignment		Chemical Shift
$Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2$	1768(w), 1729(s),	$^{13}C\{^1H\}$ NMR	μ-$O_2\underline{C}_2$	305
3a	1295(ms), 1282(ms)		μ-$\underline{C}O$	268
^{13}CO:	1730, 1686, 1260 (br)		$\underline{C}_5(CH_3)_5$	125
			$\underline{C}_5H_5$	91
			$C_5(\underline{C}H_3)_5$	11
		^1H NMR	$C_5\underline{H}_5$	4.81 (s, 10H)
			$C_5(C\underline{H}_3)_5$	1.69 (s, 30H)
$Cp^*_2Zr(O_2C_2)Fe_2Cp'_2(CO)_2$	1755(w), 1713(s),	$^{13}C\{^1H\}$ NMR	μ-$O_2\underline{C}_2$	304
3b	1287(s,br)		μ-$\underline{C}O$	269
			$\underline{C}_5(CH_3)_5$	124
			$\underline{C}_5(CH_3)H_4$	102, 92, 90
			$C_5(\underline{C}H_3)H_4$	13
			$C_5(\underline{C}H_3)_5$	11

Table 1. Continued.

Compound	Infrared ν(CO)	Assignment		Chemical Shift
		^{1}H NMR	$C_5(CH_3)\underline{H}_4$	4.79 (m, 8H)
			$C_5(C\underline{H}_3)H_4$	2.12 (s, 6H)
			$C_5(C\underline{H}_3)_5$	1.67 (s, 30H)
$Cp^*_2Zr(O_2C_2)Ru_2Cp_2(CO)_2$	1740(s), 1720(s), 1300(s)	$^{13}C\{^1H\}$ NMR	μ-$O_2\underline{C}_2$	289
3c			μ-$\underline{C}O$	250
			$\underline{C}_5(CH_3)_5$	121
			$\underline{C}_5H_5$	91
			$C_5(\underline{C}H_3)_5$	11
		^{1}H NMR	$C_5\underline{H}_5$	5.38 (s, 10H)
			$C_5(C\underline{H}_3)_5$	1.68 (s, 30H)
$Cp^*_2Zr[Cp_2Ru_2(CO)_3(CH_2)]$	1920(w), 1837(s), 1765(m),	^{1}H NMR	$C\underline{H}_2$	9.26 (s, 1H) 8.85 (s, 1H)
9	1759(s)			
			$C_5\underline{H}_5$	5.35 (s, 10H)
			$C_5(C\underline{H}_3)_5$	1.67 (s, 15H) 1.60 (s, 15H)

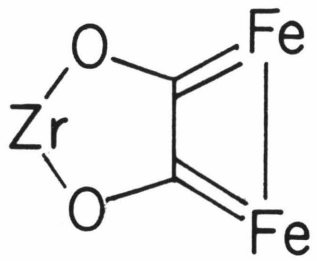
Table 1. Continued.

Compound	Infrared ν(CO)	Assignment		Chemical Shift
$\{Cp^*_2Zr\}_2O_4C_4\{CpFe\}_2$	1329(s), 1250(m), 1034(s)	^{1}H NMR	$C_5\underline{H}_5$	5.68 (s, 10H, $\nu_{(fwhm)}$ = 33 Hz)
10a				
^{13}CO:	1300, 1235, 1010		$C_5(C\underline{H}_3)_5$	1.39 (s, 60H, $\nu_{(fwhm)}$ = 6 Hz)
$\{Cp^*_2Zr\}_2O_4C_4\{CpFe\}_2$		^{1}H NMR	$C_5\underline{H}_5$	4.47 (s, 10H)
10b	1330(s), 1258(m), 1020(s)		$C_5(C\underline{H}_3)_5$	2.06 (s, 60H)

[a]NMR spectra in benzene-$\underline{d}_6$ at ambient temperature. Chemical shifts reported in δ relative to internal TMS.
[b]IR spectra obtained as nujol mulls. Values reported in cm^{-1}.

(br, unresolved)).

The structure of **3a** as determined by single crystal X-ray diffraction methods is shown in Figure 1 and the skeletal view is shown in Figure 2.[4,5] Coupling of two carbonyl ligands has given rise to the ZrO_2C_2 unit bridging the iron atoms (**A**). These seven atoms all lie approximately in the same



A

plane with a perpendicular crystallographic mirror plane containing the zirconium atom bisecting the C-C and Fe-Fe bonds. Bond angles and distances are listed in Tables 2 and 3.

Treatment of **3a** with CO (4 atm, 25°C) in benzene produces **2a** and $Cp^*_2Zr(CO)_2$, **4**, quantitatively in about one week. Under the same conditions the ruthenium analog **3c** yields **2c** and **4** in under 10 min. When ^{13}CO is used, >90% of the isotopic label is found as $Cp^*_2Zr(^{13}CO)_2$, as determined by ^{13}C NMR.

$$\underset{\textbf{3c}}{Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2} + {}^{13}CO \xrightarrow{10\ min}$$

$$\underset{\textbf{4}}{Cp^*_2Zr(^{13}CO)_2} + \underset{\textbf{2c}}{(CpRu(CO)_2)_2} \qquad (2)$$

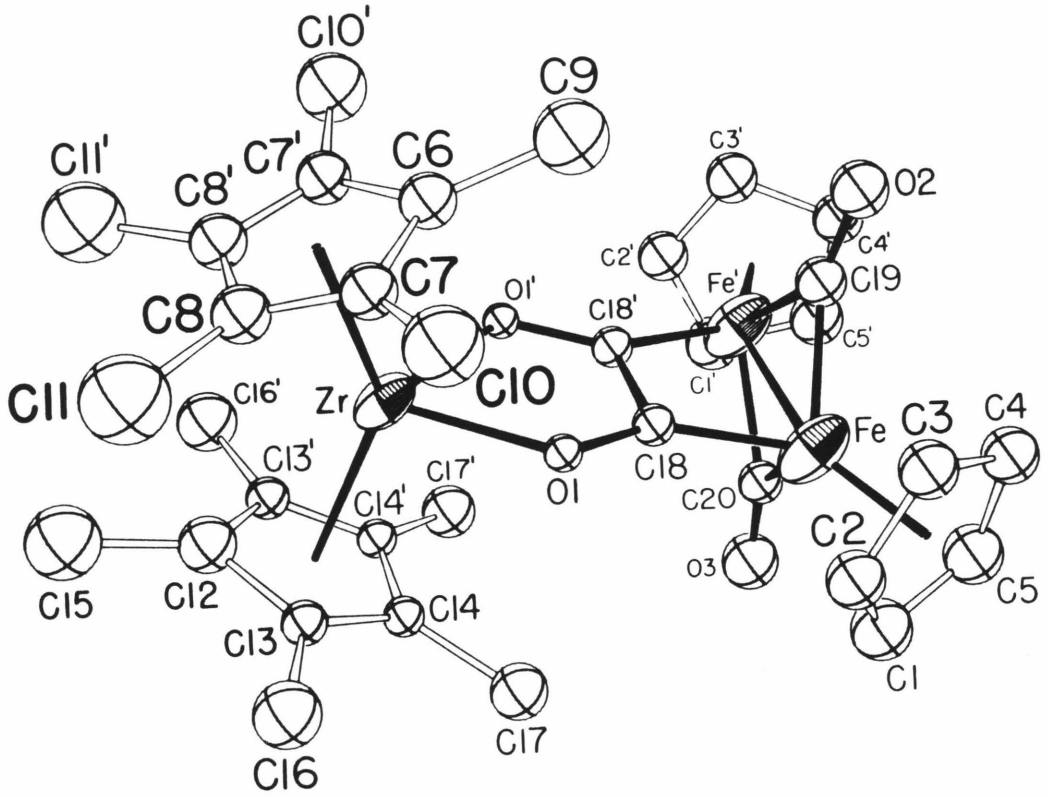


Figure 1. Molecular Configuration of $Cp^*_2Zr(O_2C_2)[CpFe(CO)]_2$, **3a.**

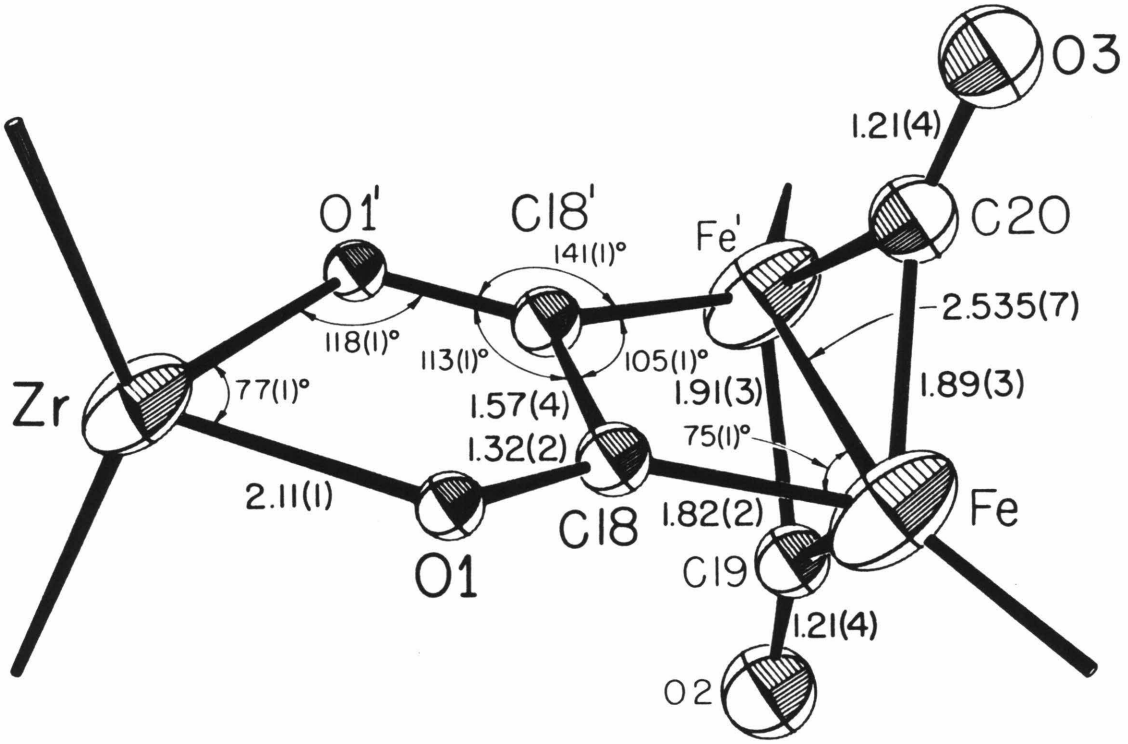


Figure 2. Skeletal view of $Cp^*_2Zr(O_2C_2)[CpFe(CO)]_2$, **3a.**

Table 2. Bond Distances in **3a** (Å).

ATOM	ATOM	DISTANCE	
Zr	01	2.11(1)	
Zr	RING1	2.23	*
Zr	RING2	2.27	*
Fe	RING3	1.76	*
Fe	Fe'	2.535(7)	
C1	C2	1.43(3)	
C2	C3	1.43(3)	
C3	C4	1.41(3)	
C4	C5	1.36(3)	
C5	C1	1.39(3)	
C6	C7	1.47(3)	
C7	C8	1.34(3)	
C8	C8'	1.42(4)	
C6	C9	1.62(5)	
C7	C10	1.56(3)	
C8	C11	1.62(4)	
C12	C13	1.46(3)	
C13	C14	1.36(3)	
C14	C14'	1.43(4)	
C12	C15	1.56(5)	
C13	C16	1.57(3)	
C14	C17	1.55(3)	
C18	C18'	1.57(4)	
C18	Fe	1.82(2)	
C18	01	1.32(2)	
C19	02	1.91(3)	
C19	02	1.21(4)	
C20	Fe	1.89(3)	
C20	03	1.21(4)	

*Ring refers to the centroid of an η^5-C_5 ring.

Table 3. Bond Angles in **3a** (deg).

ATOM	ATOM	ATOM	ANGLE	
C5	C1	C2	116(2)	
C1	C2	C3	102(2)	
C2	C3	C4	106(2)	
C3	C4	C5	115(3)	
C4	C5	C1	101(3)	
C9	C6	C7	128(1)	
C7	C6	C7'	103(3)	
C10	C7	C6	124(2)	
C10	C7	C8	126(2)	
C6	C7	C8	109(2)	
C11	C8	C7	123(2)	
C11	C8	C8'	127(1)	
C7	C8	C8'	109(1)	
C15	C12	C13	128(2)	
C13	C12	C13'	101(3)	
C16	C13	C12	123(2)	
C16	C13	C14	125(2)	
C12	C13	C14	111(2)	
C17	C14	C13	124(2)	
C17	C14	C14'	128(1)	
C13	C14	C14'	108(1)	
Fe	C18	C18'	105(1)	
Fe	C18	01	141(1)	
C18	C18'	01	113(1)	
Fe	C19	Fe	83(1)	
Fe	C19	02	138(1)	
Fe	C20	Fe	84(1)	
Fe	C20	03	138(1)	
RING1	Zr	RING2	140	*
01	Zr	01'	77(1)	
C18	Fe	C19	86(1)	
C18	Fe	C20	85(1)	
C19	Fe	C20	95(1)	

*Ring refers to the centroid of an η^5-C_5 ring.

In benzene solution a mixture of **3a** and **2b** slowly reaches equilibrium (ca. 1 week at 25°C) with **3b** and **2a** (Scheme I). Over longer periods of time (>2 weeks) new ^{1}H NMR signals consistent with $CpCp'Fe_2(CO)_4$, and $Cp^*_2Zr(O_2C_2)Fe_2CpCp'(CO)_2$ ($Cp'\equiv C_5H_4Me$) are also observed. Reaction of **3c** with **2a** results in complete conversion to **3a** and **2c**.

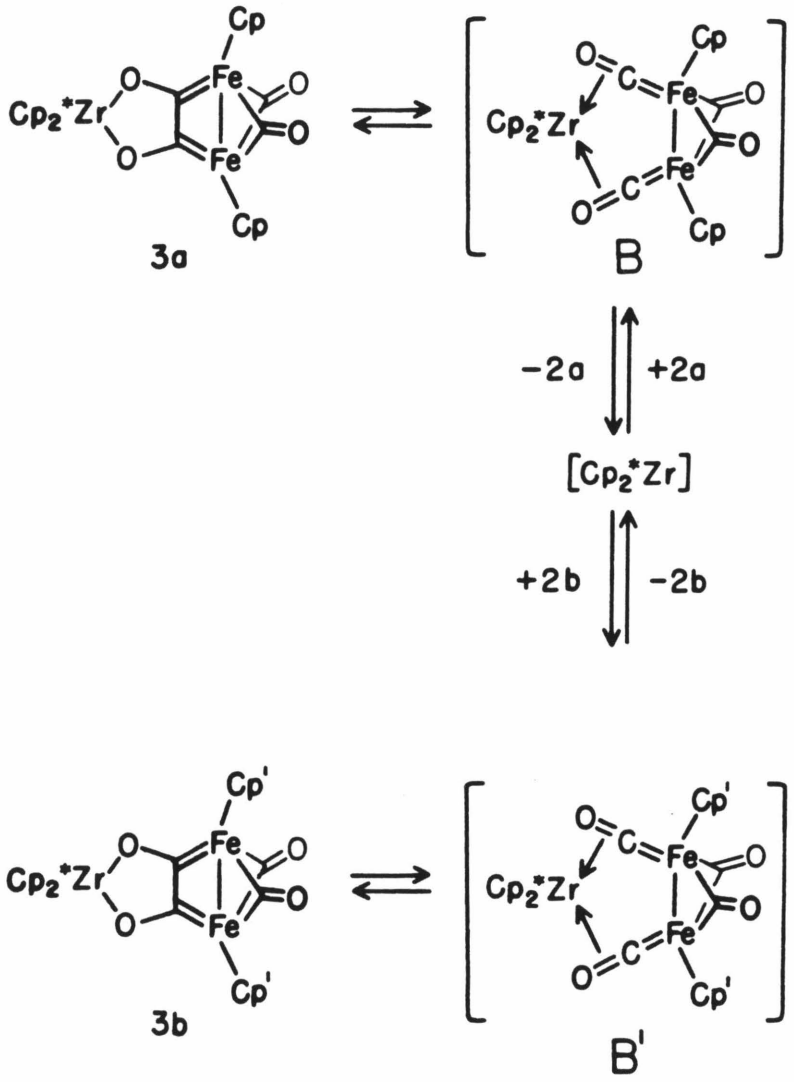
The unbridged molybdenum dimer $[CpMo(CO)_3]_2$, **5** reacts with **3a** to produc **2a** and $Cp^*_2Zr[CpMo(CO)_3]_2$, **6**, a complex in which there is no Mo-Mo bond and the two $CpMo(CO)_3$ moieties are bound to a Cp^*_2Zr center via μ_2-(C-η^1; O-η^1) carbonyl bridges.[6]

$$\underset{\textbf{3a}}{Cp^*_2Zr(O_2C_2)Cp_2Fe_2(CO)_2} + \underset{\textbf{5}}{[CpMo(CO)_3]_2} \xrightarrow{\text{seconds}} \underset{\textbf{6}}{Cp^*_2Zr[CpMo(CO)_3]_2} + \underset{\textbf{2a}}{[CpFe(CO)_2]_2} \quad (3)$$

While treatment **3a** with H_2 (4 atm, 25°C) in benzene results in decomposition to a mixture of unidentified products over one week, **3c** cleanly forms the bridging zirconoxy carbene complex $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZrHCp^*_2)$, **7** within 10 min with H_2 under the same conditions. This compound has been prepared previously from the reaction of $Cp^*_2ZrH_2$ and **2c** (see Chapter III).

$$\underset{\textbf{3c}}{Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2} + H_2 \xrightarrow{10\text{ min}} \underset{\textbf{7}}{Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZrHCp^*_2)} \quad (4)$$

Scheme I



Treatment of **3a** or **3c** with CH_3I, HCl, H_2O, Me_3SiCl, $MeSO_2CF_3$ or dimethyl acetylenedicarboxylate results in rapid decomposition. Varying amounts of **2** are observed among the products.

Compound **3a** is also produced by treatment of $Cp^*_2ZrI_2$ with $Na(CpFe(CO)_2)$ within 2 h at 25°C in benzene. No reaction is observed between $Cp^*_2ZrCl_2$ and $Na(CpFe(CO)_2)$ in benzene or DME after weeks at 25°C.

$$Cp^*_2ZrI_2 + 2\ Na(CpFe(CO)_2) \longrightarrow 2\ NaI + Cp^*_2Zr(O_2C_2)Cp_2Fe_2(CO)_2 \quad (5)$$

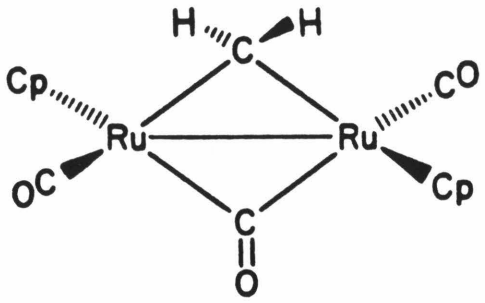
3a

Proton NMR studies show that when a mixture of cis and trans isomers of the bridging methylene complex $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, **8**, is treated with **1**, only cis-**8** is initially consumed and a new product, $Cp^*_2Zr(Cp_2Ru_2(CO)_3(CH_2))$, **9**, is formed within 20 min at 25°C (Scheme II). Excess **8** regains a cis-trans ratio of ca. 2:1 within 30 min. The ^1H NMR spectrum of **9** shows methylene resonances at δ 9.26 (1H) and 8.85 (1H), a Cp singlet at 5.35 (10H) and two Cp* singlets at 1.67 (15H) and 1.60 (15H). Four bands attributable to ν(CO) are observed in the infrared spectrum (nujol mull) of **9**: 1920(w), 1837(s), 1765(m) and 1759(s) cm^{-1}. The absence of low energy C-O stretching bands implies a different structure for **9** than found for **2a**.

Compound **9** is only slightly soluble in hydrocarbon solvents, and while apparently stable indefinitely in the solid state, solutions of **9** decompose completely within two days in benzene at 25°C to a myriad of products.

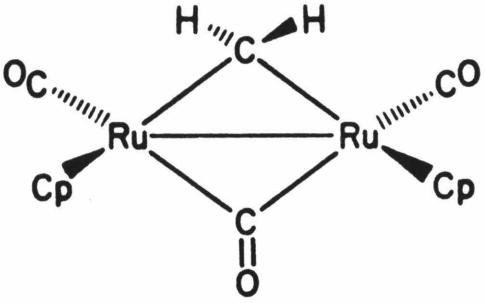
Quantitative production of **4** and **8** from **9** and CO (4 atm, 25°C)

Scheme II



trans-8

$\frac{1}{2}$ $\{Cp^*_2ZrN_2\}_2N_2$ +



cis-8

$Cp^*_2Zr[Cp_2Ru_2(CO)_3(CH_2)]$

9

requires less than 30 min and appears to be limited mainly by the rate of

$$\underset{\mathbf{9}}{Cp^*_2Zr(Cp_2Ru_2(CO)_3(CH_2))} + CO \xrightarrow{<30\ min} \underset{\mathbf{4}}{Cp^*_2Zr(CO)_2} + \underset{\mathbf{8}}{Cp_2Ru_2(CO)_3(CH_2)} \quad (6)$$

dissolution of **9** in benzene. Similarly, treatment of **9** with **2c** yields **3c** and **8** in <5 h at 25°C (eq. 7).

$$\underset{\mathbf{9}}{Cp^*_2Zr(Cp_2Ru_2(CO)_3(CH_2))} + \underset{\mathbf{2c}}{(CpRu(CO)_2)_2} \xrightarrow{<5\ h} \underset{\mathbf{3c}}{Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2} + \underset{\mathbf{8}}{Cp_2Ru_2(CO)_3(CH_2)} \quad (7)$$

Compound **3a** reacts with **1** in toluene to produce a paramagnetic complex $\{Cp^*_2Zr\}_2O_4C_4\{FeCp\}_2$, **10a**. This complex exhibits broad ^1H NMR signals at δ 5.68 (10H, ν(fwhm) = 33 Hz) and 1.39 (60H, ν(fwhm) = 6 Hz) and bands in the infrared at 1329 (s), 1250 (m), and 1034 (s) cm^{-1} (^{13}CO: 1300, 1235, and 1010 cm^{-1}). The molecular weight of **10a** as determined by ebulliometry is 1040 AMU (calcd. 1077). Magnetic susceptibility measurements show an effective magnetic moment, μeff, of 3.26 B.M. per Zr_2Fe_2 unit at 280 °K (S = 1, μ (spin only) = 2.83 B.M.). Variable temperature measurements indicate slightly antiferromagnetic behaviour with a Neel

temperature of ca. 30°K. The diamagnetic ruthenium analog, $\{Cp^*_2Zr\}_2O_4C_4\{RuCp\}_2$, **10b**, can be prepared from **1** and **3c**. Both **10a** and **10b** can be prepared by treatment of one equivalent of the dimeric **1** with the dimers **2a** and **2c**, respectively.

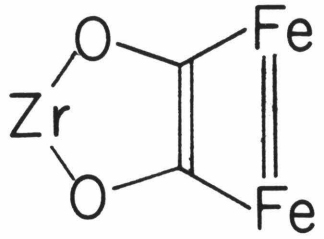
Compound **10** reacts with CO to produce insoluble products and trace amounts of **2** and **4**. These reactions are currently under investigation.

Discussion

Structure of 3a. The ZrO_2C_2 unit bridging the two iron atoms is clearly the most interesting feature of the structure of **3a**. The bond distances are in accord with the dioxozirconacyclopenta-3,4-diylidene diiron formulation indicated in **A**. The C-C bond distance (1.57(4) Å) is similar to the value found for C-C single bonds in simple hydrocarbons.[7] While the C-O distance (1.32(2) Å) is rather short for a single bond,[7] it is comparable with the C-O single bond length found for the DME molecule coordinated to a Ti(III) cation in $(Cp_2Ti(DME))^+_2(Zn_2Cl_6)^{2-}$ (1.305(8) Å).[8] That the Fe-C(carbene) distance for **3a** is 0.09 Å shorter than the Fe-C(terminal carbonyl) for cis-**2a** is also reasonable, in view of the order of bond lengths typically found for "Fischer-type" carbenes (M-C(carbene) > M-C(carbonyl)).[9] The coordination about the zirconium is normal, with the exception of the small O-Zr-O angle of 77(1)°, imposed by the five-membered ring. Stuckey's titanium-DME cation exhibits a similar angle of 76.6(2)°.[8]

An alternative resonance structure for the bridging moiety, **C**, in which there are Fe-Fe and C-C double bonds is not consistent with the

observed bond lengths. The Fe-Fe bond (2.535(7) Å) is no shorter than in cis-**2a** (2.531(2) Å). Indeed, none of the bond distances for the $CpFe(\mu\text{-}CO)_2FeCp$ moiety are statistically different from those in cis-**2a**.[10]



C

The spectral features for **3a** are readily interpretable in light of its structure. Thus the infrared bands at 1768 and 1729 cm^{-1} are attributed to the bridging carbonyls of the $Cp_2Fe_2(\mu\text{-}CO)_2$ unit (cf. 1800 and 1765 cm^{-1} for cis-**2a**)[10] and the bands at 1295 and 1282 cm^{-1} (principally) to the ν(CO) modes of the dioxozirconacyclopenta-3,4-diylidene moiety. ^{13}C NMR spectra (benzene-d_6) for **3a** show two downfield resonances, at δ 305 and 268 (1:1). ^{13}C NMR spectra of cis-**2a** at low temperatures exhibit resonances at δ 212 and 262 due to terminal and bridging carbonyls, respectively.[11] Hence the most straightforward assignment for **3a** is that the δ 268 and 305 resonances are due to the bridging carbonyl and carbene carbons.

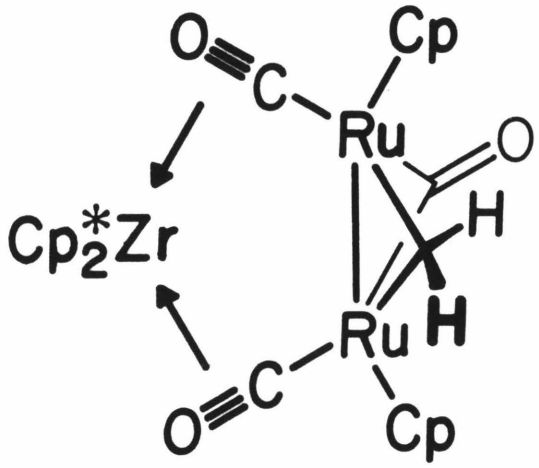
Compound **3c**, the ruthenium analog of **3a**, has a similar carbonyl-coupled structure. As in **3a**, a broad low energy band at 1300 cm^{-1} in the infrared spectrum is found for the O_2C_2 bridge, in addition to stretches at 1740 and 1720 cm^{-1} for the carbonyls bridging the two ruthenium atoms. The

downfield resonances at δ 289 and 250 in the ^{13}C NMR spectra for **3c** can be assigned to the O_2C_2 and bridging carbonyl carbons.[12]

The Carbonyl Coupling Reaction. The formation of **3** may be viewed as a reductive coupling of the two terminal carbonyl ligands of **2** with oxidation of zirconium from the divalent to tetravalent state. In this respect reaction **1** may be likened to the reductive coupling of aldehydes[4] and terminal olefins[14] by permethylzirconocene. While radial pathways cannot be excluded, it is likely that all of these processes involve intramolecular coupling of two π-bound ligands. Indeed, there is precedent for "side-on" π-bonding between early transition metals and bridging carbonyl ligands.[3,15]

While a complex held together by only μ-(C-η^1; C,O-η^2) bridging carbonyls as in **B** is not precedented, the structure of **9**, the product of the reaction of **1** with the bridging methylene complex cis-**8**, raises some intriguing questions. It is the absence of the low energy ν(CO) bands in the infrared spectrum of **9** that rules out a structure analogous to **3a**. The ^1H NMR spectrum of **9** exhibits signals due to inequivalent methylene protons, a single Cp resonance, and a pair of inequivalent Cp* signals. The four bands between 1920 and 1759 cm^{-1} in the infrared spectrum are not especially helpful, except in eliminating a O_2C_2 bridge from consideration. We favor the structure analogous to **B** shown below. In this complex a zirconium(II) center is coordinating to the two terminal carbonyl ligands of cis-**8** in a π-fashion. Infrared bands for π-bound carbonyls have been reported from 1560 to 1683 cm^{-1}.[3,15] While the stretches observed for **9** fall outside of this domain, there is reason to believe the Zr-carbonyl interactions may be weaker than in these cases. In all of the previously observed structures of π-bound

carbonyls direct bonds between the metals add to the stability of the carbonyl bridge. In addition, the wide "bite" of the cis-$Ru_2(CO)_2$ chelate in **D** may result in less than optimal Zr-carbonyl interactions. Such a weakened interaction would result in higher stretching frequencies for the carbonyl ligands in **D**.



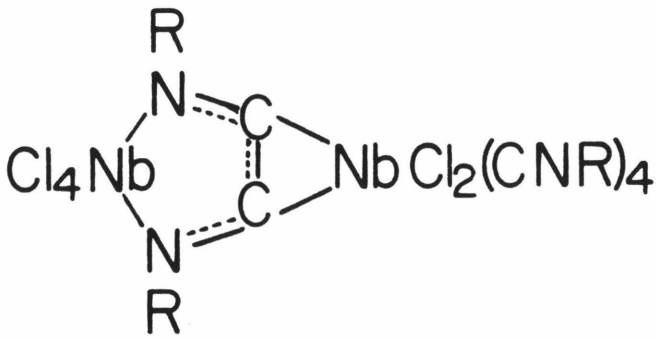
D

It is not possible to rule out less symmetrical structures which are fluxional on the NMR time scale. The low solubility of **9** has prevented low temperature studies. In considering such structures, it must be taken into account that **1** reacts only with cis-**8**. In addition, the rapid substitution chemistry of **9** requires a structure which readily releases **8**. Structure **D** seems the most straightforward proposal in all of these regards.

It is significant that permethylzirconocene forms a complex with an apparently intact metal carbonyl dimer such as cis-**8** without carbonyl coupling. It is difficult to explain this fact on the basis of structural

differences between cis-**8** and **2c**. The structure of a related μ-alkylidene complex of ruthenium, cis-$Cp_2Ru_2(CO)_3(CMe_2)$[16] exhibits a Ru-Ru bond length (2.712(1) Å) essentially identical to that found in trans-**2c** (2.72 Å).[17] In addition, the disposition of the cis terminal carbonyls in this compound is not significantly different from that found in cis-**2a**.[10] On the other hand, the different structures of **3** and **9** can be justified on the basis of electronic arguments. Replacement of one carbonyl by a methylene group in **8** results in additional π-backbonding to the remaining carbonyl ligands. The increased electron density on the terminal carbonyls would render the reductive coupling less favorable. In keeping with this proposal, the observed carbonyl stretching frequencies for **8** are found at lower energies than in **2c**.[18]

Other processes involving the reductive coupling of ligands have been reported. Lippard and coworkers have studied the coupling of adjacent isocyanides in a seven-coordinate molybenum complex.[19] In this case the reductant is zinc metal and the product upon hydrolysis is a molybdenum-bound bis(alkylamino)acetylene. A similar process has been suggested in the formation of a diniobium complex. The structure of $Nb_2Cl_6(t\text{-BuNC})_4$-(μ-t-BuNCCN-t-Bu), **11**, reported by Cotton amd Roth,[20] apparently arises from the coupling of cis isocyanides. While the mechanism of formation is uncertain, the $C_2(NR)_2Nb$ moiety bears a strong resemblance to the C_2O_2Zr unit in **3a**. Bond orders >1 along the N-C-C-N frame, however, suggest significant differences. The structure analogous to **A** in the dinuclear **11** would be a metallacyclopropadiene. It is not surprising that this hypothetical ring is not observed and that the electrons are distributed in a different manner along the reduced ligand framework than in **A**. However, comparison



11

with **A** does raise the interesting question as to whether an unsaturated metal center would insert into a Nb-C bond in **11** to produce a dimetallacyclobutadiene structure.

It is also significant that the two niobium atoms have such different environments. The $NbCl_4$ unit should be Lewis acidic in much the same manner as is a zirconium(IV) center. The $NbCl_2(CNR)_4$ center, however, is relatively electron rich. This observation is perhaps the only factor in common between **3**, these two coupled-isocyanide cases and two additional reports of carbon-carbon bond formation <u>via</u> reduction of ligands. Lukehart[21] and Cramer[22] have published work describing C-C bond formation in boron-iron and uranium-iron complexes. The mechanisms of these transformation are unclear, but both products contain oxygen substituted allyl ligands bound to iron centers. The presence of five-membered rings containing Lewis acids bound to heteroatoms in **3**, **11** and these systems suggests that chelation may play an important role in positioning ligands prior to reductive bond

formation.

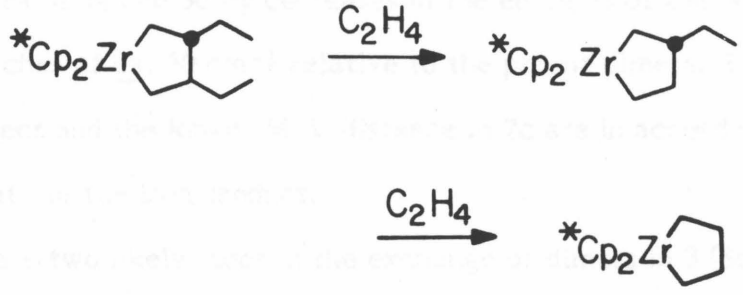
Discussion of one other related system is in order. Casey and coworkers have recently reported the crystal structures of $Cp_2Zr(CpM(CO)_2)_2$ (**12a:** M = Fe, **12b:** M = Ru).[23] These compounds contain two separate $CpM(CO)_2$ units bound via unbridged M-M bonds to the zirconium. Compound **12** is prepared by treatment of Cp_2ZrI_2 with two equivalents of $Na(CpM(CO)_2)$. This is in striking contrast to the analogous reaction in the Cp* system (eq. 5) in which **3a** is produced. These different results can be understood by consideration of the steric and electronic differences between Cp_2Zr and Cp_2^*Zr systems. The larger steric bulk of the Cp* rings would favor a larger separation between the metals and associated ligands. This is the case in **3** where there are three intervening atoms between the metals. In addition, the greater electron donating properties of the permethyl rings will result in a higher electron density on the zirconium in the Cp^*_2Zr fragment than in Cp_2Zr. The lower oxidation state in **12** (formally Zr(II)) is thus less well suited to the permethyl ring system. The interesting question of which structural mode will be adopted by the complexes with partially methylated rings is currently being studied by Casey and coworkers.[23]

Reversibility of the Coupling Process. In an effort to exploit the C-C bond formation in the carbonyl coupling process we have explored the reactivity of these compounds. The first experiment that often comes to mind in these laboratories is treatment of a new compound with carbon monoxide. Coupling of carbenes with CO is a well documented process,[24-26] and since the diferracyclobutadiene moiety may very well be a strained species, we had hoped to find incorporation of CO into **3** with release of that strain. In

fact, **3**, reacts with CO to cleanly produce $Cp^*_2Zr(CO)_2$, **4**, and **2**. Compound **4** contains formally divalent zirconium, thus this transformation requires transfer of two electrons back to the zirconium from the $O_2C_2Fe_2$ unit. The fact that labeled CO is incorporated only into **4** shows that the O_2C_2 bridge uncouples and remains on the iron atoms as carbonyl ligands. These observations suggest that the formation of **3** from **2** and $Cp^*_2Zr(II)$ is reversible. In agreement, we find that an equilibrium between **2a, 3a, 2b** and **3b** is slowly established in benzene solution (25°C, >1 week (Scheme I)).

The observation of the mixed complexes $Cp'CpFe_2(CO)_4$ and $Cp^*_2Zr(O_2C_2)Fe_2CpCp'(CO)_2$ after longer reaction times may not be due to any role played by the zirconium species. A 1:1 mixture of **2a** and **2b** scrambles to a statistical mixture of **2a, 2b** and $Cp'CpFe_2(CO)_4$ within 30 days at 25°C in benzene. This scrambling is almost four-fold faster in the presence of ca. 0.1 equivalent of $Na(CpFe(CO)_2)\cdot THF$. No efforts were made to exclude ambient light from any of these experiments.

The equilibrium between **3a** and the π-complex **B** in Scheme I bears a resemblance to the rapid metallacyclopentane and bis(olefin) complex interconversions observed in nickel,[27] titanium,[27] and zirconium[14] systems. In the latter, Erwin and Bercaw[14] observed the stepwise reaction of ethylene



(8)

and 3,4-diethylzirconacyclopentane, $Cp^*_2ZrCH_2CHEtCHEtCH_2$ to $Cp^*_2ZrCH_2CH_2CHEtCH_2$ and subsequently to $Cp^*_2ZrCH_2CH_2CH_2CH_2$ with release of 1-butene (eq. 8).

It is significant that **2a** will completely displace the ruthenium dimer in **3c** to form **3a**, indicating that **3a** is the thermodynamic product (eq. 9). The reasons for this preference may be two-fold: (1) the M-M bond in **2c** is

$$\underset{\textbf{3c}}{Cp^*_2Zr(O_2C_2)Ru_2Cp_2(CO)_2} + \underset{\textbf{2a}}{(CpFe(CO)_2)_2} \rightleftharpoons \underset{\textbf{3a}}{Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2} + \underset{\textbf{2c}}{(CpRu(CO)_2)_2} \quad (9)$$

ca. 0.2 Å longer than in **2a** or **3a**. If this distance persists in **3c** it might further destabilize the dimetallacyclobutadiene fragment, and (2) any process which increases electron density at the metals would be less favorable in the case of ruthenium vs. iron. While the reductive coupling of the terminal carbonyls does not formally change the oxidation states of the metals in the dimer, an effective increase in electron density occurs with the loss of some of the π-accepting properties of the carbonyls. This is evidenced in the infrared spectra of **3a** and **3c** by decreases in the energies of the bridging carbonyl stretches of ca. 30 cm^{-1} relative to the parent dimers. Both this electronic effect and the longer M-M distance in **2c** are in accord with the greater stability of the iron product.

There are two likely steps in the exchange of dimers in **3** (Scheme I and eq. 9). First the O_2C_2 unit must uncouple, and second the dimer must

dissociate from the zirconium. The rate of dimer substitution is roughly the same for the exchange of **2b** with **3a** and **2a** with **3c**, despite the driving force for the latter. This suggests that uncomplexed permethylzirconocene is produced at comparable rates for **3a** and **3c**. In contrast to the dimer exchange reactions, **3c** reacts with CO to produce **4** and **2c** ca. 10^3 times faster than the analogous carbonylation of **3a**, suggesting that the rapid carbonylation of **3c** (and possibly the slower reaction of **3a**) does not proceed via trapping of uncomplexed permethylzirconocene by CO. While it does not seem likely that CO would accelerate the rate of the uncoupling step, an associative substitution process on the π-complex **B** is feasible. Based on the data it is not possible to conclude whether the uncoupling step is faster in **3c** or if **2a** and **2c** have significantly different ligating abilities in the π-complex. While the carbonylation may proceed associatively, the steric constraints of the Cp* rings should preclude interaction of a second dimer with **B**, rendering the dimer exchange process dissociative.

The reversibility of the carbonyl coupling process is manifested in other reactions of **3**. While **3a** decomposes slowly under H_2 (4 atm, 25°C), **3c** is cleanly converted to the bridging zirconoxy carbene complex $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZrHCp^*_2)$,[28] **7**, in <10 min. The reaction of $Cp^*_2ZrH_2$ with **2c** also yields **7**. Thus it seems likely that H_2 reacts with **3c** to yield $Cp^*_2ZrH_2$ and **2c** which then react further to produce **7**. However, as in the carbonylation, the short reaction time implies that dissociation of **2c** from **3c** is promoted by H_2.

The reaction of the iron complex **3a** with CO, H_2, and **2b** are all relatively slow, requiring ca. one week at 25°C. A notable deviation from

this pattern is found in the reaction of **3a** with $(CpMo(CO)_3)_2$, **5**. In this instance production of **2a** and $Cp^*_2Zr(CpMo(CO)_3)_2$, **6**, in solution occurs within seconds. Compound **6**, prepared previously from the reaction of **1** with **5**,[6] is best described as a Cp^*_2Zr dication coordinated to the carbonyl oxygens of two $CpMo(CO)_3$ anions. Thus the reaction of **1** with **5** results in reduction of the Mo-Mo bond, rather than reductive carbonyl coupling.

While it seems feasible that small molecules such as H_2 and CO might associate with **3c** whereas the dimer **2a** is too large, it is difficult to rationalize the extremely rapid reaction of **3a** with **5** in terms of an associative substitution process. As an alternative explanation we favor an outer sphere electron transfer from either **3a** or the π-bound intermediate **B** to the molybdenum dimer to produce $(CpMo(CO)_3)_2^-$ and a zirconium(III) cation. Rapid dissociation of **2a**, perhaps assisted by the opposite charge on the molybdenum species, followed by a second electron transfer and collapse would lead to **6** (Scheme IV). Outer sphere transfer of two electrons to yield a zirconium(IV) dication and two $CpMo(CO)_3$ anions is also a possibility, although this is less attractive as it requires formation of greater charge separation in a solvent with a relatively low dielectric constant such as benzene.

Reaction of Other Metal Carbonyl Complexes with 1. In an attempt to extend this carbonyl coupling process beyond $(CpM(CO)_2)_2$ complexes, we have studied the reactions of **1** with other metal carbonyl compounds. The complexes $M_3(CO)_{12}$ (M = Fe, Ru, Os) were treated with **1** in hydrocarbon solvents under various conditions. In all cases light orange powders were

isolated which exhibited a myriad of Cp* resonances in the ^1H NMR spectra. Infrared spectra of these materials showed several broad bands clustered around 2000 and 1700 cm^{-1}. No lower energy bands attributable to carbonyl coupled products were observed. $H_2Os_3(CO)_{10}$ and $[CpNi(CO)]_2$ reacted with **1** similarly. None of these reaction products were pursued further.

The observation was made, however, that when excess **1** was used in preparing **3**, yields and purity were diminished. When **3a** is treated with **1** in toluene at 25°C, dark crystals of $\{Cp^*_2Zr\}_2O_4C_4\{CpFe\}_2$, **10a**, can be isolated in moderate yield from the brown solution. These crystals dissolve to give red-brown solutions which exhibit broad singlets at δ 5.68 (10H) and 1.39 (60H) in the ^1H NMR spectrum. Three significant bands are observed in the infrared spectrum: 1329(s), 1250(m), 1034(s) cm^{-1} (^{13}CO: 1300, 1235,

$$\underset{\mathbf{1}}{1/2\{Cp^*_2ZrN_2\}_2N_2} + \underset{\mathbf{3a,c}}{Cp^*_2Zr(O_2C_2)Cp_2M_2(CO)_2} \longrightarrow 3/2\ N_2 + \underset{\mathbf{10a,b}}{\{Cp^*_2Zr\}_2O_4C_4\{CpM\}_2} \qquad (10)$$

and 1010 cm^{-1}). No higher energy ν(CO) bands are observed.

The extremely broad ^1H NMR resonances [Cp: ν(fwhm) = 33 Hz, Cp*: ν(fwhm) = 6 Hz] found for **10a** suggest that this complex is paramagnetic. This is confirmed by susceptibililty measurements indicating μeff = 3.26 B.M. per Zr_2Fe_2 unit at 280°K [(S = 1, μ (spin only) = 2.83 B.M.). The susceptibility and low temperature antiferromagnetic behavior[29] are not

readily interpretable without further structural information for **10a.**

Green crystals of $\{Cp^*_2Zr\}_2O_4C_4\{RuCp\}_2$, **10b**, can be isolated in 30-40% yield from the reaction of **1** with **3c**. The ^1H NMR spectrum of **10b** exhibits singlets at δ 4.47 (10H) and 2.06 (60H). In this case, however, both resonances are quite sharp (ν(fwhm) < 1 Hz) and susceptibility measurements show that the complex is diamagnetic. The infrared spectrum of **10b** is virtually identical with **10a**, with three bands at 1330(s), 1258(m), and 1020(s) cm^{-1}. Single crystals of **10b** have been grown, but they do not appear to diffract in an X-ray beam. Attempts to grow crystals of **10a** and **10b** suitable for a structure determination are proceeding. In lieu of better structural information, it is necessary to speculate on the basis of spectral data. The singlets observed in the ^1H NMR spectra of **10** for the Cp* protons broaden somewhat at lower temperatures, but no splitting is observed down to -100°C. This indicates that either the four Cp* rings have equivalent environments, or that a very facile fluxional process is occurring. The same is true for the Cp protons. From the absence of any bands above 1300 cm^{-1} in the infrared spectra it can be concluded that the complexes contain no typical terminal or bridging carbonyl ligands. Three reasonable structures (Fig. 4) can be drawn for complexes derived from **3** <u>via</u> a second carbonyl coupling step. Structure **I** is analogous to **3**, except that both pairs of carbonyl ligands have been coupled to form two planar dimetallacyclobutadiene rings. In structure **II** the O_2C_2 moieties are turned 90° to yield tetrahedral bridges similar to the arrangement often found for acetylenes bound to metal dimers. Structure **III** contains one of each O_2C_2 bridge geometry, and phenomenologically is the result of coupling the two bridge carbonyls in **3** with

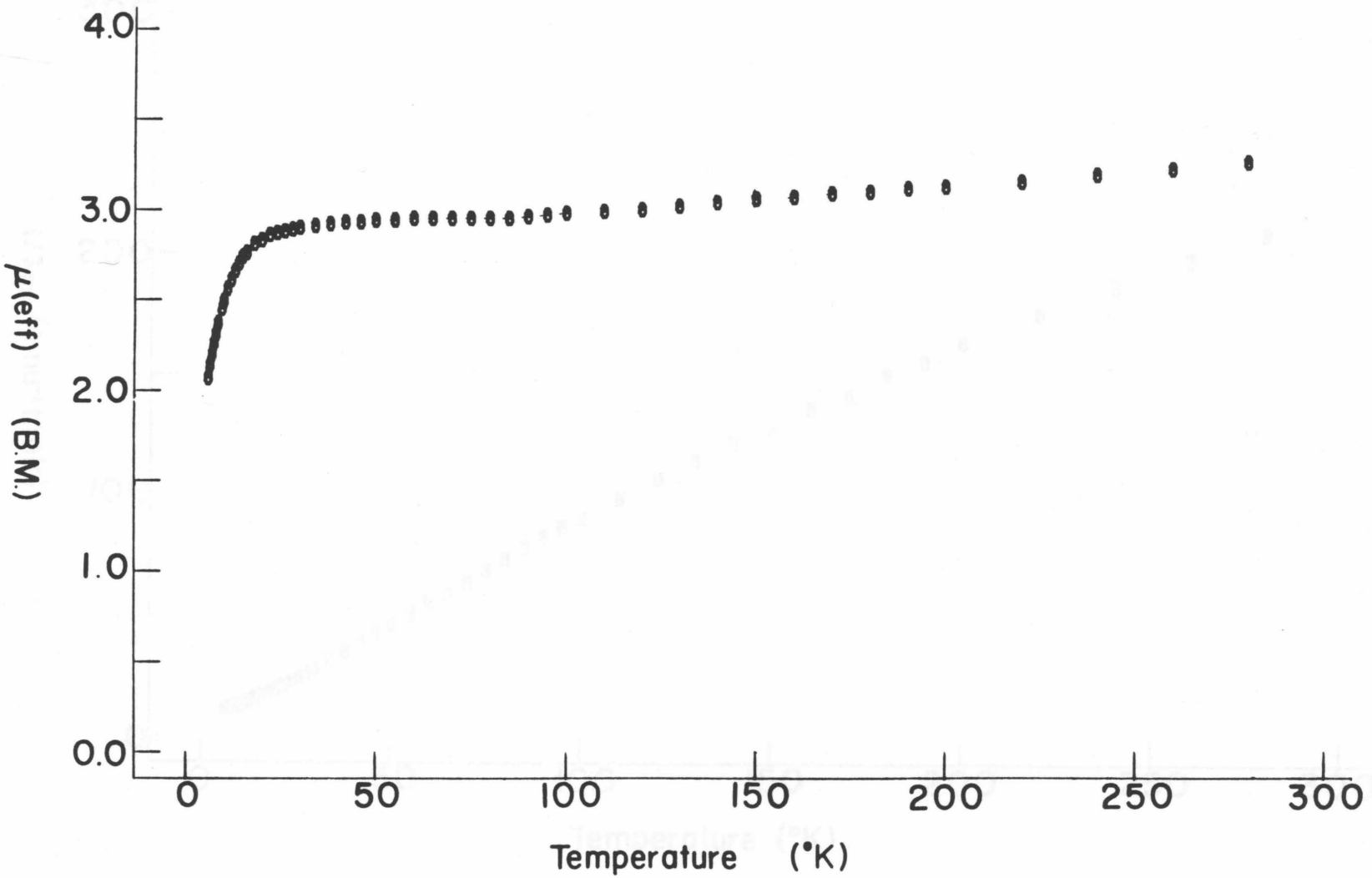


Figure 3. Plot of μ(eff) vs. T for $\{Cp^*_2Zr\}O_4C_4\{CpFe\}_2$, **10a.**

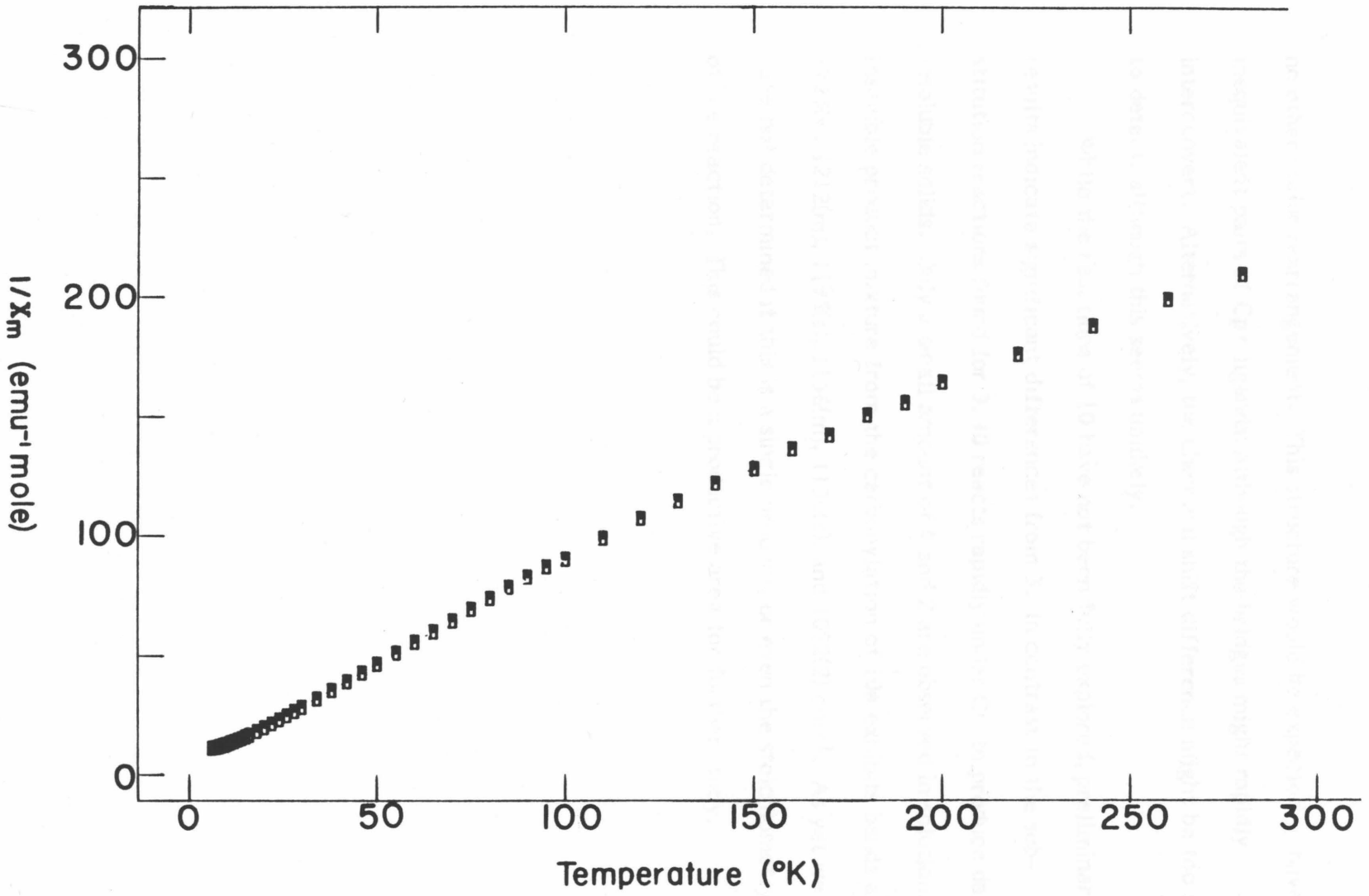
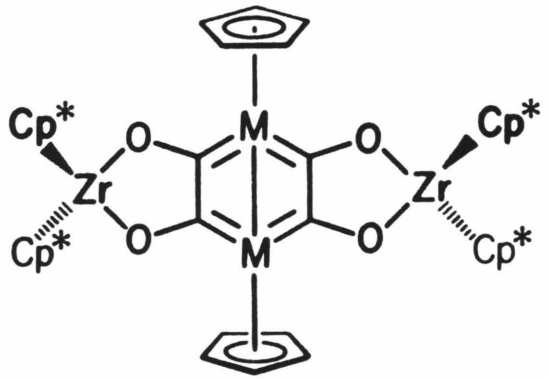


Figure 4. Plot of $1/\chi$ vs. T for $\{Cp^*_2Zr\}O_4C_4\{CpFe\}_2$, **10a.**

no other major rearrangement. This structure would be expected to have inequivalent pairs of Cp* ligands, although the bridges might rapidly interconvert. Alternatively, the chemical shift difference might be too small to detect, although this seems unlikely.

While the reactions of **10** have not been fully explored, preliminary results indicate significant differences from **3**. In contrast to the substitution reactions found for **3**, **10** reacts rapidly under CO to produce dark insoluble solids. Only a small amount of **4** and **2** are observed in solution. The insoluble product mixture from the carbonylation of **10a** exhibits bands at 1725(s), 1212(m), 1195(s), 1156(m), 1130(s), and 1092(2) cm^{-1}. As yet we have not determined if this is a single product, or even the stoichiometry of the reaction. This could be a productive area for further study.



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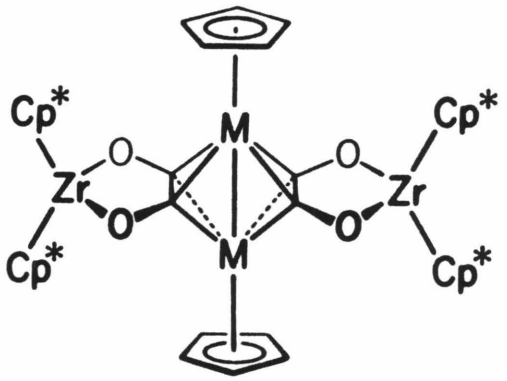
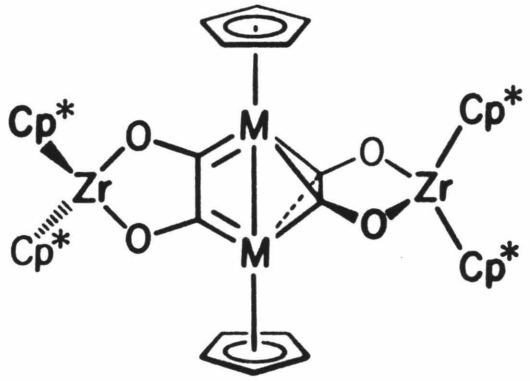


II



III

Figure 5. Three possible structures for $\{Cp^*_2Zr\}O_4C_4\{CpM\}_2$, **10.**

Experimental Section

General Considerations. All manipulations were performed using either glove box or high vacuum line techniques. Hydrocarbon solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[31] NMR solvents, benzene-$\underline{d}_6$ and toluene-$\underline{d}_8$ were also purified by transfer from "titanocene". Hydrogen was passed through MnO on vermiculite and then over 4 Å molecular sieves.[32] Carbon monoxide (MCB) was used directly from the cylinder. $\{Cp^*_2ZrN_2\}_2N_2$,[33] $(CpFe(CO)_2)_2$,[34] $(CpRu(CO)_2)_2$,[35,36] $Cp_2Ru_2(CO)_3(CH_2)$,[28] $(CpMo(CO)_3)_2$,[37] and $((C_5H_4Me)Fe(CO)_2)_2$[34] were prepared as described previously.

Infrared spectra were measured on a Beckman 4240 spectrophotometer. ^1H NMR spectra were obtained using Varian EM-390 or JEOL FX-90Q spectrometers. ^{13}C NMR spectra were obtained using the JEOL FX-90Q instrument. Samples for ^{13}C NMR experiments were generally prepared with ^{13}CO enriched $(CpRu(CO)_2)_2$[38] and $(CpFe(CO)_2)_2$ and ca. 0.1 M added $Cr(acac)_3$[11] to facilitate observation of the carbonyl carbons. Elemental analyses were performed by Bernhardt Microanalytical Laboratory, Dornis and Kolbe Microanalytical Laboratory, or by Larry Henling at the CIT analytical service.

$Cp^*_2Zr(O_2C_2)Fe_2Cp_2(CO)_2$, 3a. A solution of 1 (285 mg, 0.353 mmol) and **2a** (250 mg, 0.707 mmol) in 50 mL toluene was stirred under vacuum for 2 h at 25°C. Toepler pump analysis of the gases generated showed 1.04 mmol (98.2%) of non-combustible gas, presumed to be dinitrogen. Recrystallization of the residue from toluene/petroleum ether yielded 265 mg (53%) dark brown crystals.

Anal. calcd. for $C_{34}H_{40}Fe_2O_4Zr$: C, 57.07; H, 5.64; Zr, 12.75. Found: C, 56.94; H, 5.71; Zr, 12.54.

$Cp^*_2Zr(O_2C_2)Ru_2Cp_2(CO)_2$, 3c. A solution of 1 (264 mg, 0.33 mmol) and **2c** (255 mg, 0.57 mmol) in 40 mL benzene was stirred for 1 h at 25°C. The resulting metallic orange solid was collected by filtration and washed once with 3 mL benzene, yielding 144 mg (31%) of solid. The orange-black residue was recrystallized from toluene/petroleum ether to yield a second crop of 180 mg (39%). ^1H NMR indicates these products contain ca. 0.5 moles of benzene or toluene as solvent of crystallization, which can be removed by stirring a slurry **3c** in petroleum ether overnight, filtering and drying in vacuo.

Anal. calcd. for $C_{34}H_{40}O_4Ru_2Zr$: C, 50.66; H, 5.00; Zr, 11.32. Found: C, 50.92; H, 5.20; Zr, 10.80.

$Cp^*_2ZrRu_2Cp_2(CO)_3(CH_2)$, 9. A slurry of 1 (205 mg, 0.254 mmol) and **8** (209 mg, 0.486 mmol) in 10 mL toluene was stirred 2 h at 25°C, cooled to -80°C and filtered. The solid was washed with 5 mL petroleum ether and dried in vacuo, yielding 287 mg (75%) of red-orange solid.

Anal calcd. for $C_{34}H_{42}O_3Ru_2Zr$: C, 51.56; H, 5.35. Found: C, 52.05; H, 5.48.

$Cp^*_2ZrI_2$. A slurry of $Cp^*_2ZrCl_2$ (2.3 g, 5.3 mmol) and BI_3 (1.4 g, 3.6 mmol) in 20 mL toluene was stirred for 4 h at 25°C. The solvent was then removed and the yellow solid dried in vacuo for 1 h. Recrystallization from diethyl ether yielded 2.73 g (88%) of pure, crystalline product.

Anal. calcd. for $C_{20}H_{30}I_2Zr$: C, 39.03; H, 4.91. Found: C, 39.27; H, 4.85.

Reaction of $Cp^*_2ZrI_2$ with $Na(CpFe(CO)_2)\cdot THF$. $Cp^*_2ZrI_2$ (32 mg, 0.052 mmol), $Na(CpFe(CO)_2)\cdot THF$ (30 mg, 0.110 mmol) and 0.3 mL benzene-d_6 were added to an NMR tube and the tube sealed with a torch. Formation of **3a** over a period of 2 h was accompanied by a color change from bright yellow to red-brown and formation of precipitate.

Reaction of 3c with ^{13}CO. Compound **3c** (18 mg, 0.022 mmol) and benzene-d_6 (0.3 mL) were added to an NMR tube, ^{13}CO (120 torr, 77°K, ca. 2 mL) introduced and the tube sealed. A ^1H NMR spectrum observed after 10 min showed only $Cp^*_2Zr(CO)_2$ and **2c**. A ^{13}C NMR spectrum showed >90% enrichment in the carbonyl carbons of $Cp^*_2Zr(CO)_2$ (δ 275).

Reaction of 3c with H_2. Compound **3c** (10 mg, 0.012 mmol) and benzene-d_6 (0.3 mL) were added to an NMR tube, H_2 (700 torr, 77°K, ca. 2 mL) introduced and the tube sealed. A ^1H NMR spectrum observed after 10 min showed complete conversion to $Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)$, as confirmed by comparison with a spectrum of an authentic sample.

Reaction of 3a with $(CpMo(CO)_3)_2$. Compound **3a** (15 mg, 0.021 mmol) and $(CpMo(CO)_3)$ (10 mg, 0.020 mmol) were added to an NMR tube. Upon addition of benzene-d_6 (0.3 mL) a rapid reaction ensued with a color change from brown to dark red. The tube was sealed with a latex septum. The ^1H NMR spectrum showed conversion to **2a** and $Cp^*_2Zr(CpMo(CO)_3)_2$, as confirmed by comparison with spectra of the authentic compounds.

Reaction of 3c with 2a. Compound **3c** (14 mg, 0.017 mmol), **2a** (6 mg, 0.017 mmol) and benzene-d_6 were sealed in an NMR tube. After ten days the ^1H NMR spectrum showed conversion to **3a** and **2c**.

Reaction of 3a with 2b. Compound **3a** (10 mg, 0.014 mmol), **2b** (5 mg,

0.013 mmol) and benzene-$\underline{d}_6$ were sealed in an NMR tube. After one week the ^{1}H NMR spectrum showed a mixture of **3a**, **3b**, **2a**, and **2b**. After two weeks additional signals for $Cp^*_2Zr(O_2C_2)Fe_2(CO)_2CpCp'$ and $CpCp'Fe(CO)_4$ were observed.

$\{Cp^*_2Zr\}_2O_4C_4\{CpFe\}_2$, 10a. A solution of **1** (490 mg, 0.607 mmol) and **2a** (210 mg, 0.587 mmol) in 40 mL toluene was stirred for 2 h at 25°C, filtered and the solvent volume reduced to 10 mL. The solution was stirred at -80°C for 1 h, filtered and the residue washed once with 2 mL toluene, once with petroleum ether and then dried <u>in vacuo</u> for 3 h. 286 mg (45%) of black crystals were collected. Proton NMR analysis indicated the product is solvated with toluene (1:1). Analysis of the filtrate showed a <u>ca.</u> 1:1 mixture of **3a** and **12a**. Additional **1** (100 mg, 0.124 mmol) was dissolved with the filtrate in 30 mL toluene and the solution was stirred for 1 h. Removal of solvent followed by addition of 10 mL petroleum ether yielded a red solution with brown-black solid. The solid as collected on a frit and washed three times with 10 mL petroleum ether, yielding 193 mg (31%) of product.

<u>Anal.</u> calcd. for $C_{54}H_{70}Fe_2O_4Zr_2 \cdot C_7H_8$: C, 62.65; H, 6.72. Found: C, 62.35; H, 6.52.

$\{Cp^*_2Zr\}_2O_4C_4\{CpRu\}_2$, 10b. A slurry of **1** (570 mg, 0.644 mmol) and **2c** (230 mg, 0.518 mmol) in 10 mL toluene was stirred at 25°C for 5 h. Removal of solvent and addition of petroleum ether followed by filtration, yield gray crude product. Recrystallization from toluene yielded 245 mg (41%) of green solid. Proton NMR analysis indicated somewhat less than 1 toluene of crystallization.

<u>Anal.</u> calcd. for $C_{54}H_{70}O_4Ru_2Zr_2 \cdot C_7H_8$: C, 58.15; H, 6.24. Found:

C, 57.33; H, 6.10.

Magnetic Susceptibility Measurements. Variable temperature magnetic susceptibility measurements were made at the University of Southern California SQUID-based S.H.E. Corp. magnetic susceptometer. A diamagnetic correction for **10a** of $\chi_d = -1.21 \times 10^{-3}$ was applied. This value was calculated from the measured diamagnetic susceptibility of the ruthenium analog **10b** ($\chi_d = -1.17 \times 10^{-3}$), corrected for Ru-Fe differences found for **2a** and **2c**. The susceptibility of **10a** was also measured at 298°K (2.98 B.M.) using the Evans method.[39]

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CHAPTER III

Reversible Reduction of Coordinated Carbon Monoxide by Permethylzirconocene Hydride Complexes. Characterization and Reactivity of a Bridging Diruthenium Zirconoxy Carbene Complexes.

Introduction

Our interest in complexes containing the permethylzirconocene moiety and later transition metals has led us to several new structural and reactivity modes for carbonyl complexes. In the course of investigating the reaction chemistry of $Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2$ ($Cp^* \equiv \eta^5$-$C_5(CH_3)_5$) , a complex in which the terminal carbonyl ligands have been reductively coupled, an interesting reaction was observed.[1a] Reaction of the ruthenium complex with hydrogen quantitatively yielded a new complex in which a carbonyl ligand has been reduced by addition of a zirconium hydride. Previous studies have shown that the carbonyl coupled products are in equilibrium with zirconocene and simple dinuclear carbonyl complexes.[1] Combined with the fact that permethylzirconocene rapidly reacts with hydrogen to form a dihydride, this suggested to us that a study of the reactions of zirconium hydrides with $(CpRu(CO)_2)_2$ was in order.

Following the discovery in these laboratories that $(C_5Me_5)_2ZrH_2$, 1, reacts with CO to yield a variety of products, studies were undertaken to elucidate the mechanism of what was at the time the only homogeneous reduction of CO by a transition metal hydride complex. These studies have been summarized elsewhere,[2] but a key finding was the fact that 1 will react with terminal carbonyl ligands to produce "zirconoxy" carbenes (eq. 1). Zirconoxy carbenes have been observed in the reaction of zirconium

$$L_nM\text{–}CO + Cp^*_2ZrH_2 \longrightarrow L_nM{=}C(H)OZr(H)Cp^*_2 \qquad (1)$$

hydride complexes with $Cp_2M(CO)$ (M = Cr, Mo, W),[3] $Cp_2NbR(CO)$ (R = H, alkyl, phenyl),[3] $Cp_2Zr(PMe_3)(CO)$[4] and $CpM(CO)_2$ (M = Co, Rh).[5]

Reported in this chapter are the synthesis and characterization of zirconoxy carbenes which bridge two ruthenium atoms. This is the first instance of a zirconoxy carbene which occupies a bridging position. The addition of the zirconium hydride across the bound carbonyl is shown to be reversible. Furthermore, the fluxionality of the diruthenium fragment is proposed to occur through an intermediate in which the carbene occupies a terminal position. Lewis acids are shown to induce C-O bond cleavage in the carbene, with subsequent transfer of a second zirconium hydride and production of a methylene bridge. These studies suggested the conditions in which $LiHBEt_3$ can be used to effect the transformation of a bridging carbonyl to a bridging methylene ligand directly.

Results

$Cp^*_2ZrH_2$, **1**, reacts with $(CpRu(CO)_2)_2$, **2**, rapidly at 25°C in hydrocarbon solvents to yield <u>trans</u>-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZr(H)Cp^*_2)$, **3**. This compound is fluxional and exhibits temperature dependent ^1H NMR

$$\underset{\mathbf{1}}{Cp^*_2ZrH_2} + \underset{\mathbf{2}}{(CpRu(CO)_2)_2} \longrightarrow \underset{\mathbf{3}}{Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)} \qquad (2)$$

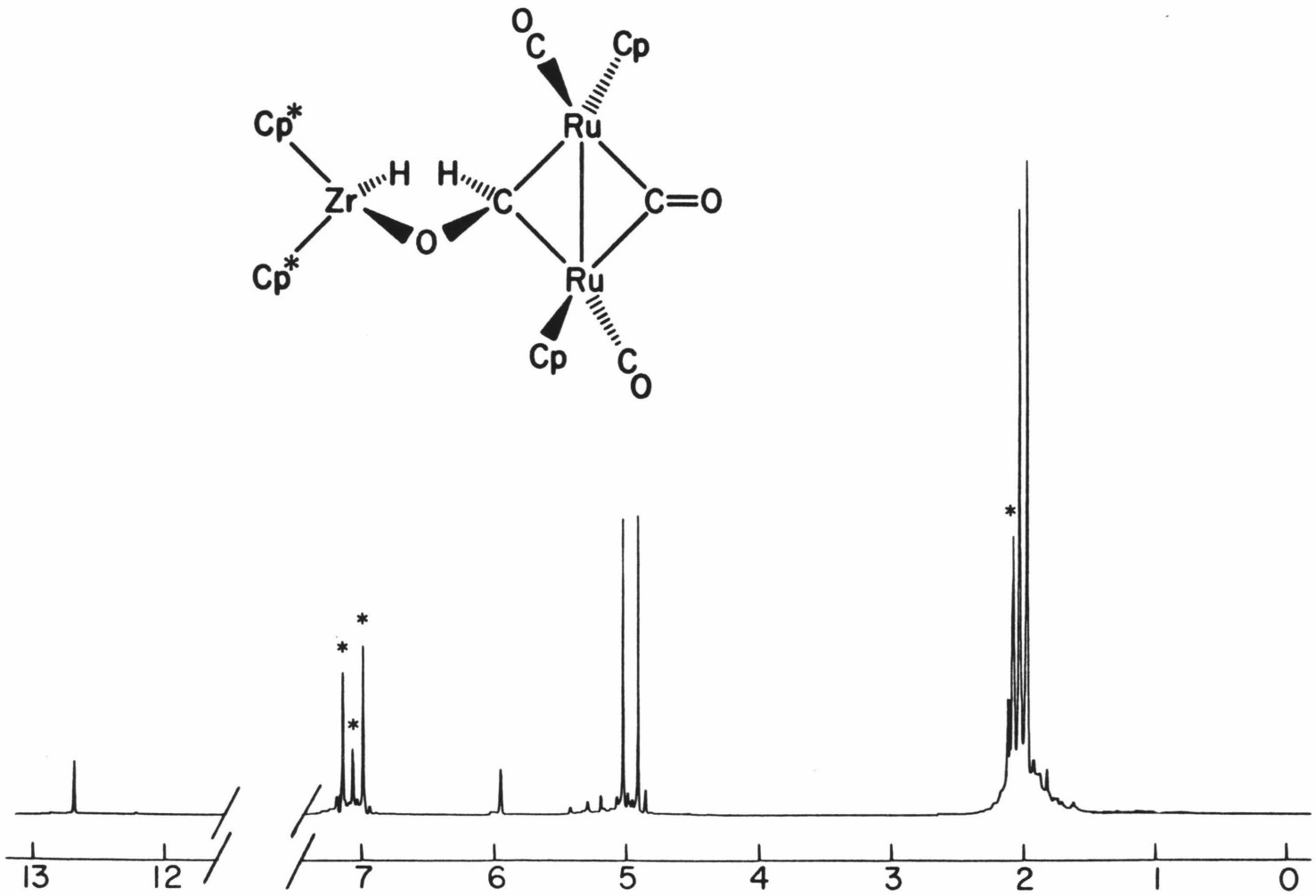


Figure 1. 500 MHz ^{1}H NMR spectrum of $Cp_2Ru_2(CO)_3[C(H)OZrHCp^*_2]$, **3**, at 172 K, toluene-d_8 solvent. Asterisks denote resonances due to solvent.

Table 1. NMR[a] and IR[b] Data.

Compound	IR	Assignment		Chemical Shift
$Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)$		^1H NMR[c]	ZrOC(H)	12.75 (s, 1H)
3	$\nu(CO)$: 1929(s),1771(s),		Zr-H	6.10 (s, 1H)
	1108(s)		C_5H_5	5.04 (s, 10H)
			$C_5(CH_3)_5$	2.01 (s, 30H)
		^1H NMR[d]	ZrOC(H)	12.67 (s, 1H)
			Zr-H	5.94 (s, 1H)
			C_5H_5	4.98 (s, 5H) 4.85 (s, 5H)
			$C_5(CH_3)_5$	2.04 (s, 15H) 1.95 (s, 15H)
		$^{13}C\{^1H\}$[d]	μ-CO	248
			Ru-CO	203 201
			ZrO-C(H)	192 (J_{CH} = 153)
			$C_5(CH_3)_5$	118 117

Table 1. Continued.

Compound	IR	Assignment		Chemical Shift
			$\underline{C}_5H_5$	95 92
			$C_5(\underline{C}H_3)_5$	12
$Cp_2Ru_2(CO)_3(C(H)ZrClCp^*_2)$[e]		^1H NMR[c]	Zr$OC(\underline{H})$	12.60 (s, 1H)
5			$C_5\underline{H}_5$	5.14 (s, 10H)
			$C_5(C\underline{H}_3)_5$	1.94 (s, 30H)
		^1H NMR[d,f]	Zr$OC(\underline{H})$	12.73 (s, 1H)[h] 12.59 (s, 1H)[g]
			$C_5\underline{H}_5$	5.37 (s, 5H)[g] 5.28 (s, 5H)[h] 4.86 (s, 5H)[g] 4.79 (s, 5H)[h]
			$C_5(CH_3)5$	1.85 (s, broad)[g,h]
$Cp_2Ru_2(CO)_3(C(H)OZr(OH)Cp^*_2)$		^1H NMR[c]	Zr$OC(\underline{H})$	12.65 (s, 1H)
6	$\nu_{(CO)}$: 1925(s), 1770(s),		$C_5\underline{H}_5$	5.15 (s, 10H)

Table 1. Continued.

Compound	IR	Assignment	Chemical Shift
	1100(s,br)	ZrO<u>H</u>	4.25 (s, 1H)
	ν(OH): 3675(w)	$C_5(C\underline{H}_3)_5$	1.86 (s, 30H)

[a]Chemical shifts reported in δ relative to internal TMS. [b]Spectra obtained as nujol mulls. Values reported in cm^{-1}. [c]Toluene-$\underline{d}_8$ solvent, ambient temperature. [d]Toluene-$\underline{d}_8$ solvent, -70°C. [e]Compound **5** was not isolated. [f]At -70°C **5** exists as a mixture of two isomers in a 3:1 ratio, denoted by g and h. [g]Major isomer. [h]Minor isomer.

spectra. In the low temperature limit (Fig. 1) resonances are found at 12.67 and 5.90 ppm for the carbene and zirconium hydride protons, with two resonances each for inequivalent Cp and Cp* ligands. These signals coalesce into single Cp and Cp* resonances upon warming. Based upon a coalescence temperature of -4°C for the Cp at 90MHz, $\Delta G^{\ddagger}$ for ring equilibration is 14.0(2) kcal·mol^{-1}. In the hafnium analog, **4**, synthesized from **2** and $Cp^*_2HfH_2$, $\Delta G^{\ddagger}$ is 14.4(2) kcal·mol^{-1} at 5°C.

The infrared spectrum of **3** (nujol mull) shows strong bands at 1929, 1771, and 1108 cm^{-1}. The ^{13}C NMR spectrum observed at -70°C shows carbonyl resonances at 201, 203 and 248 ppm. The latter is consistent with a bridging carbonyl and the former two with terminal ligands. In the ^{1}H coupled spectru, the carbene carbon appears as a doublet at 192 ppm (J_{CH} = 153 Hz). In addition, pairs of Cp and Cp* resonances are observed. Upon warming the three carbonyl signals coalesce, disappearing into the baseline. While the carbene signal broadens significantly, then sharpens above room temperature, the C-H coupling constant is virtually the same at 50°C (J_{CH} = 154 Hz) as it is at -70°C.

Cp^*_2ZrHCl reacts with **2** in about one day at 25°C to form **5**, the chloride analog of **3**. Compound **5** also exhibits a temperature dependent ^{1}H NMR, with the Cp appearing as a very broad signal at 25°C, separating into two signals below 10°C. Upon further cooling each Cp resonance separates into two peaks in roughly 1:3 ratios. Similarly, the carbene proton resonance separates into peaks at 12.75 and 12.59 (ca. 3:1). Threlkel reported a similar observation in the low temperature ^{13}C NMR spectrum of $Cp_2Nb(H)(C(H)OZrHCp^*_2)$ and ascribed it to two different rotomers about

the C-O bond of the zirconoxy carbene.[6]

A second equivalent of **1** can attack **3** to give what appears to be $Cp_2Ru_2(CO)_2(\mu\text{-}C(H)OZrHCp^*_2)_2$. This compound is insoluble in hydrocarbon solvents, but exhibits bands in the infrared at 1913 and 1058 cm^{-1}, consistent with a <u>trans</u> structure with two bridging carbenes and two terminal carbonyls. No further characterization has been attempted. As a result of this side reaction, preparation of **3** is best carried out with a slow addition of **1** to a solution of **2**. This is most conveniently accomplished by the action of hydrogen on the carbonyl coupled product $Cp^*_2Zr(O_2C_2)$-$Cp_2Ru_2(CO)_2$.[1] This produces **3** cleanly with no excess **1** present.

Compound **3** decomposes in benzene solution at 25°C over a period of weeks to many unidentified products. This process takes hours at 80°C. In the presence of 4 atm of H_2 at 25°C neither the rate nor products of this decomposition are significantly changed. With D_2 under the same conditions,

$$\underset{\mathbf{3}}{Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)} \xrightarrow{D_2} \underset{\underline{d}_2\text{-}\mathbf{3}}{Cp_2Ru_2(CO)_3(C(D)OZrDCp^*_2)} \qquad (3)$$

however, both the hydride and carbene positions are deuterated ($t_{1/2}$ ~3 h). Compound **3** reacts under 4 atm of carbon monoxide at 25°C in 14 hours to

$$\underset{\mathbf{3}}{Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)} \xrightarrow{CO} Cp^*_2Zr(CO)_2 + \underset{\mathbf{2}}{(CpRu(CO)_2)_2} + H_2 \qquad (4)$$

yield $Cp^*_2Zr(CO)_2$, **2** and presumably H_2.

Reaction with CH_3I results in rapid formation of methane and the iodide analog of **3**, which then reacts further with CH_3I to produce $Cp^*_2ZrI_2$ and **2** over a period of several days.

Compound **3** reacts with H_2O in benzene to yield H_2 and the hydroxy complex $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZr(OH)Cp^*_2)$, **6**. The ^1H NMR spectrum of **6** at 25°C shows resonances at 12.64 and 4.35 ppm attributable to carbene and hydroxide protons, as well as singlets for the Cp and Cp* ligands. The O-H stretch is observed at 3675 cm^{-1}. Compound **6** is considerably more thermally stable than **3**, with complete decomposition requiring heating at 55°C for 2.5 weeks in benzene. While the ^1H NMR spectrum of this pyrolysis shows a myriad of Cp* signals, greater than 95% of the ruthenium is present as **2** and $CpRu(CO)_2H$ in a 1:1.25 molar ratio.

While protonation of **3** with CF_3COOH results in formation of $Cp^*_2Zr(OOCCF_3)_2$ and **2** <u>via</u> $Cp_2Ru_2(CO)_3(C(H)OZr(OOCCF_3)Cp^*_2)$, reaction of CF_3COOH with the latter species is nearly as fast as with **3**.

Compound **3** reacts with $HBF_4 \cdot Me_2O$ in benzene at 25°C to rapidly yield the known bridging methylene complex $Cp_2Ru_2(CO)_3(CH_2)$, **7**, as a

$$\underset{\mathbf{3}}{Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)} + HBF_4 \cdot Me_2O \longrightarrow \underset{\mathbf{7}}{Cp_2Ru_2(CO)_3(CH_2)} + \ldots \qquad (5)$$

mixture of <u>cis</u> and <u>trans</u> isomers. A single Cp* containing product, as yet unidentified, is also obtained. Using <u>d_2</u>-**3**, this reaction produces <u>d_2</u>-**7**

initially. Compound **7** is also formed from **3** and $BF_3 \cdot Et_2O$ in benzene.

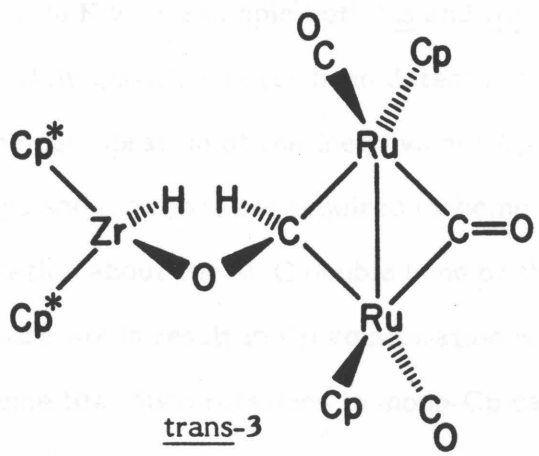
Compound **7** is the major product in the reaction of **2** and $LiHBEt_3$ in

$$\underset{\mathbf{2}}{[CpRu(CO)_2]_2} + LiHBEt_3 \xrightarrow{\text{toluene}} \underset{\mathbf{7}}{Cp_2Ru_2(CO)_3(CH_2)} \qquad (6)$$

toluene, and can be isolated in 60% yield. No **7** is formed if this reaction is run in THF instead of toluene. The known iron analog of **7** could not be synthesized in this manner.

Discussion

Structure and Fluxional Behavior of $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)OZr(H)Cp^*_2)$. On the basis of NMR data, **3** can be shown to have the trans structure pictured below. Low temperature ^{13}C NMR data (Table 1) are particularly indicative in this determination: (1) Assignment of the zirconoxy



trans-**3**

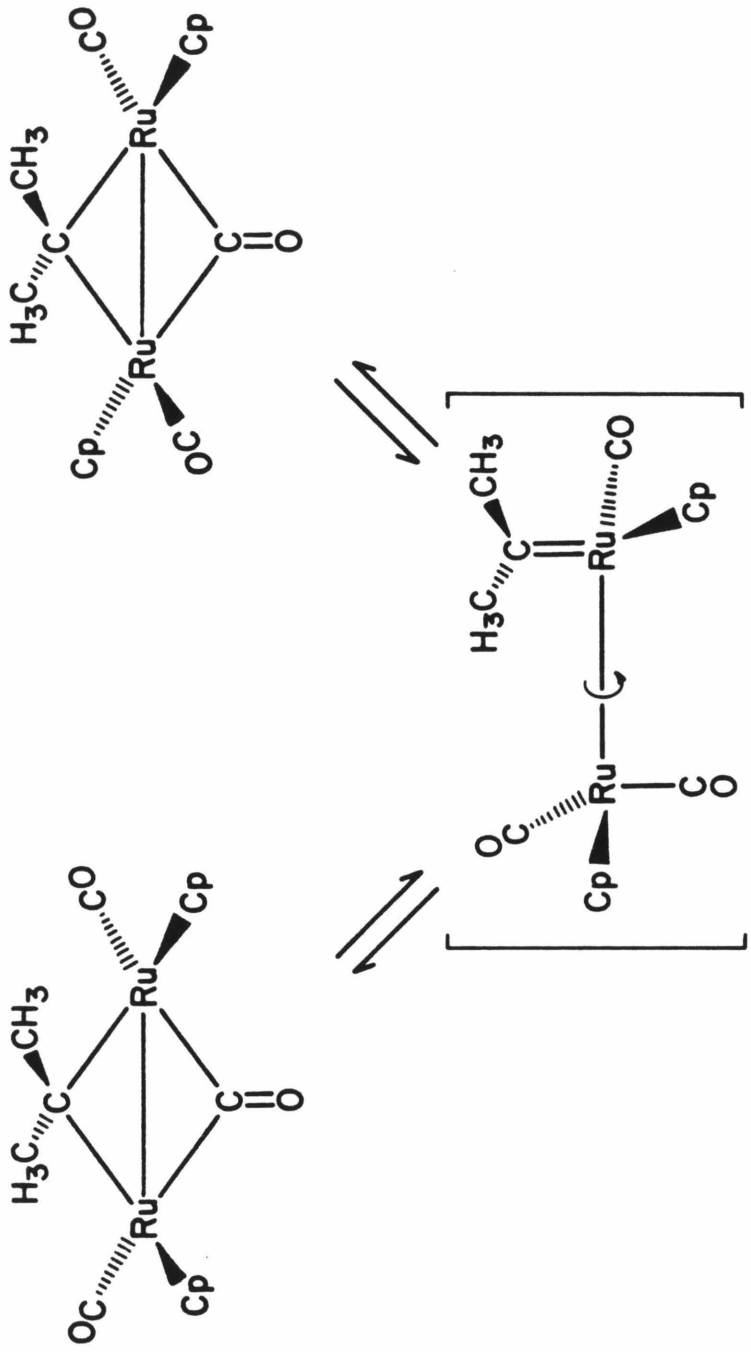
carbene to the bridging position is supported by the presence of resonances for two terminal carbonyls (201 and 203 ppm) and only a single bridging carbonyl (248 ppm).[7] (2) The trans disposition of the Cp rings and terminal carbonyls about the Ru-Ru bond is mandated by the low temperature NMR data also. In the cis form the two Cp rings would be equivalent, appearing as a single resonance. In fact, two singlets are observed in both the ^{13}C and ^{1}H NMR spectra at low temperatures, as expected for the trans arrangement.

The chemical shifts for the zirconium hydride and carbene proton signals are near or within the characteristic ranges.[3] The C-H coupling constant of 153 Hz for the carbene is somewhat larger than the 136 Hz reported by Threlkel for a terminal niobium zirconoxy carbene,[3] implying more p character in the C-H bond of the latter.

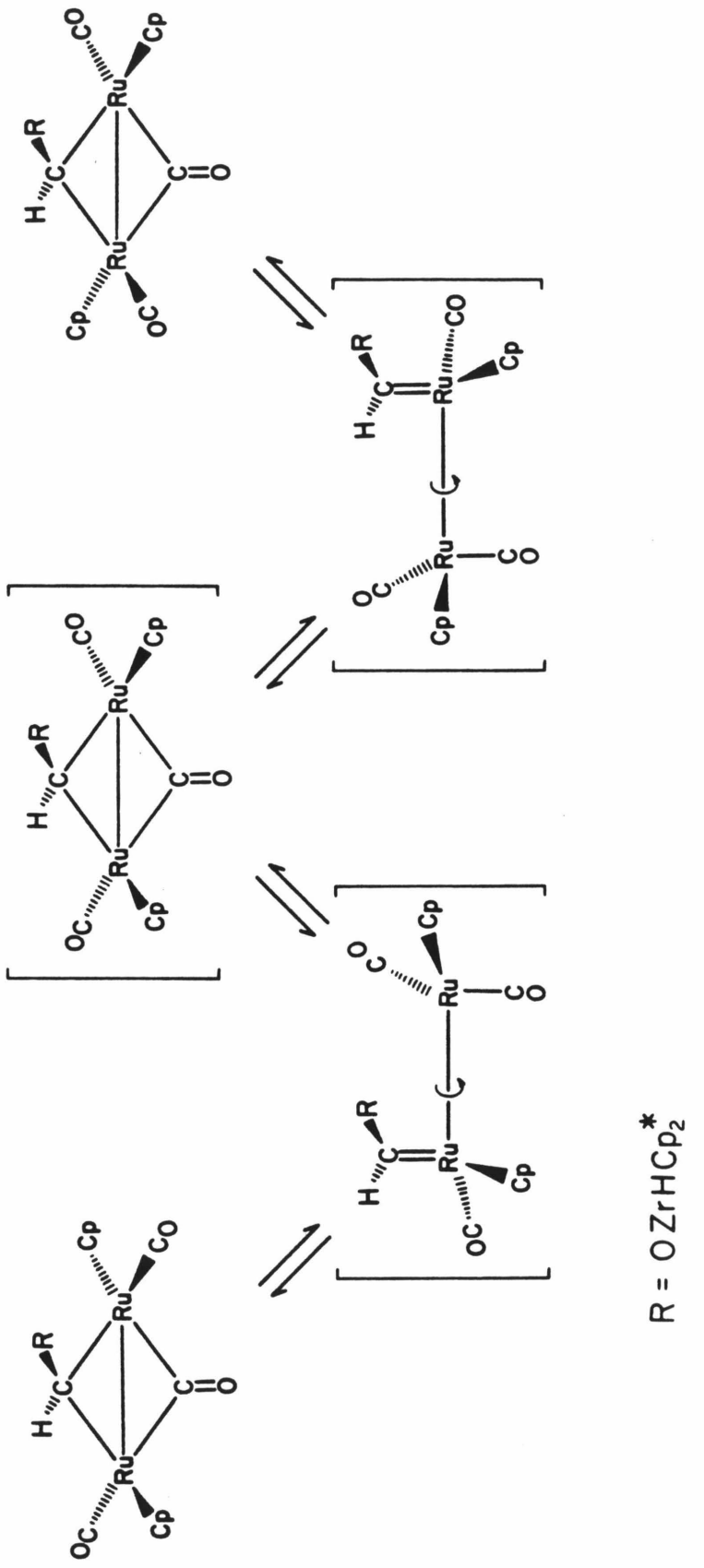
That **3** exhibits fluxional behavior is not surprising in light of similar observations for bridging alkylidenes of iron,[8] ruthenium,[9] and cobalt.[10] In a logical extension of the exhaustive studies of Cotton,[11] Roberts, [12], Gansow[13] and coworkers, Knox has suggested the bridged terminal equilibrium shown in Scheme I to explain the cis-trans isomerization of a bridging isopropylidene complex.[9] While it is reasonable that **3** is undergoing such a process, one distinction must be made. In Knox's example both cis and trans isomers are observed in equilibrium, while cis-**3** has never been detected. The process under consideration is the equilibration of the inequivalent Cp rings, in which two bridge openings and rotations are required (Scheme II).

Alternatively, rotation about the M-C double bond of the terminal carbene followed by closure would result in Cp equilibration with only a single opening step (Scheme III). Such rotations in mono-Cp carbene

Scheme I



Scheme II

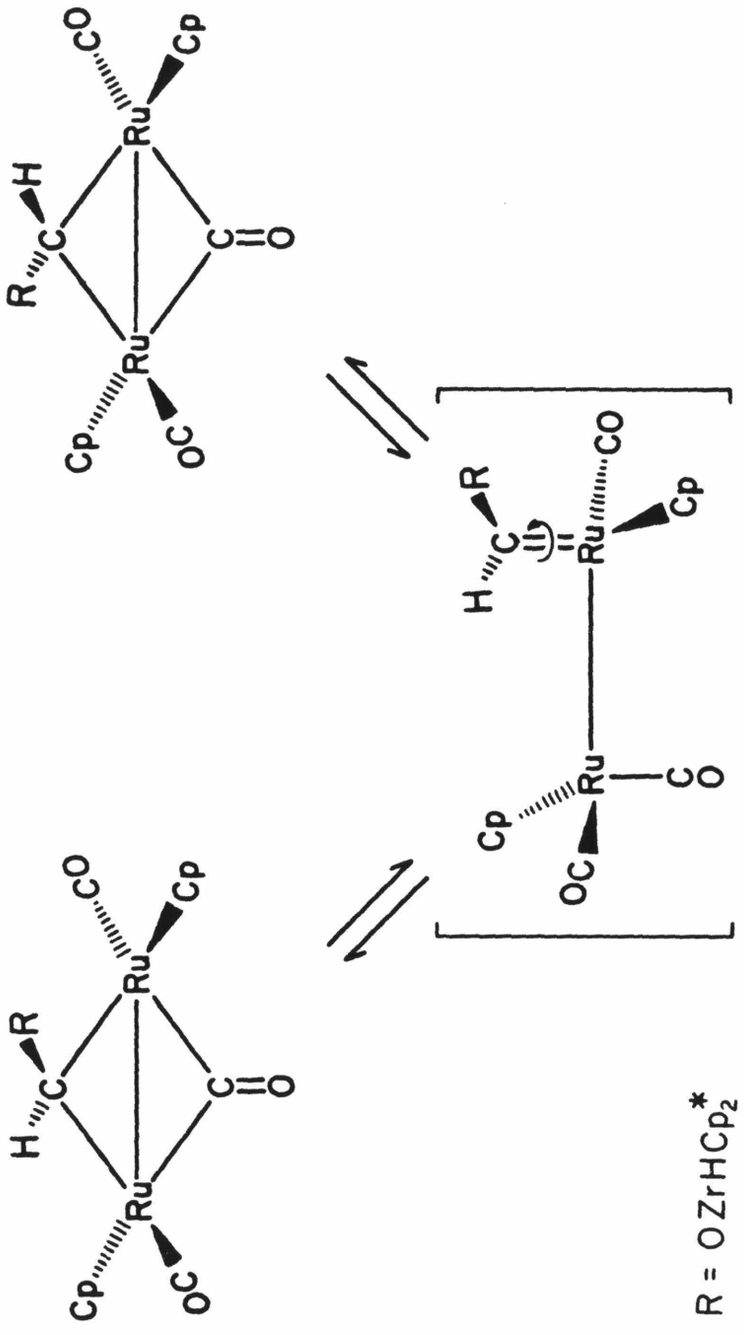


complexes appear to be facile. Fischer and coworkers report that while in the solid state structure of $CpMn(CO)_2(=CMe_2)$ the isopropylidene ligand is in the "vertical" configuration with inequivalent methyl groups, only single resonances are observed in the ^1H and ^{13}C NMR spectra at -55°C.[14,15] This implies rapid rotation around the Mn-C double bond, although there is insufficient information to quantify the barrier. Rapid rotation at -55°C is in agreement with theoretical work published by Fenske and Kostic for which the two-fold alkylidene rotation barrier in $CpMn(CO)_2(=CMe_2)$ was calculated to be ca. 9 kcal·mol^{-1}.[16] In the case of the purely carbonyl system **2**, Gansow has shown that pairwise carbonyl bridge opening is rate limiting with $\Delta G^{\ddagger}$ = 7.6 kcal·mol^{-1}.[13] In the same study the rotational barrier around the Ru-Ru bond was estimated at less than 5 kcal·mol^{-1}.

Knox reports an activation energy of ca. 20 kcal·mol^{-1} at 100°C for cis-trans isomerization.[9] In addition, Bergman and Theopold report activation energies of ca. 17 kcal·mol^{-1} for the cis-trans isomerizations of $Cp_2Co_2(CO)_2(\mu\text{-}C(H)(neo\text{-}C_5H_{11})$ and $Cp_2CoRh(CO)_2(\mu\text{-}CH_2)$.[10,17] The lower values at ca. 0°C of 14.0 for **3** and 14.4 kcal·mol^{-1} for the hafnium analog **4** may in part be due to stabilization of the terminal carbene intermediate relative to the bridging carbene by the zirconoxy substituent. Such stabilization would lower the bridged-terminal carbene exchange barrier in both Schemes II and III. In addition, the barrier to carbene rotation should also be lower in the case of a zirconoxy carbene, due to the decrease in M-C bond order associated with resonance forms available to heteroatom carbenes.

A third mechanism for Cp equilibration in **3** is shown in Scheme IV. A hydrogen shift from the carbene back to the zirconium produces a symmetrical

Scheme III



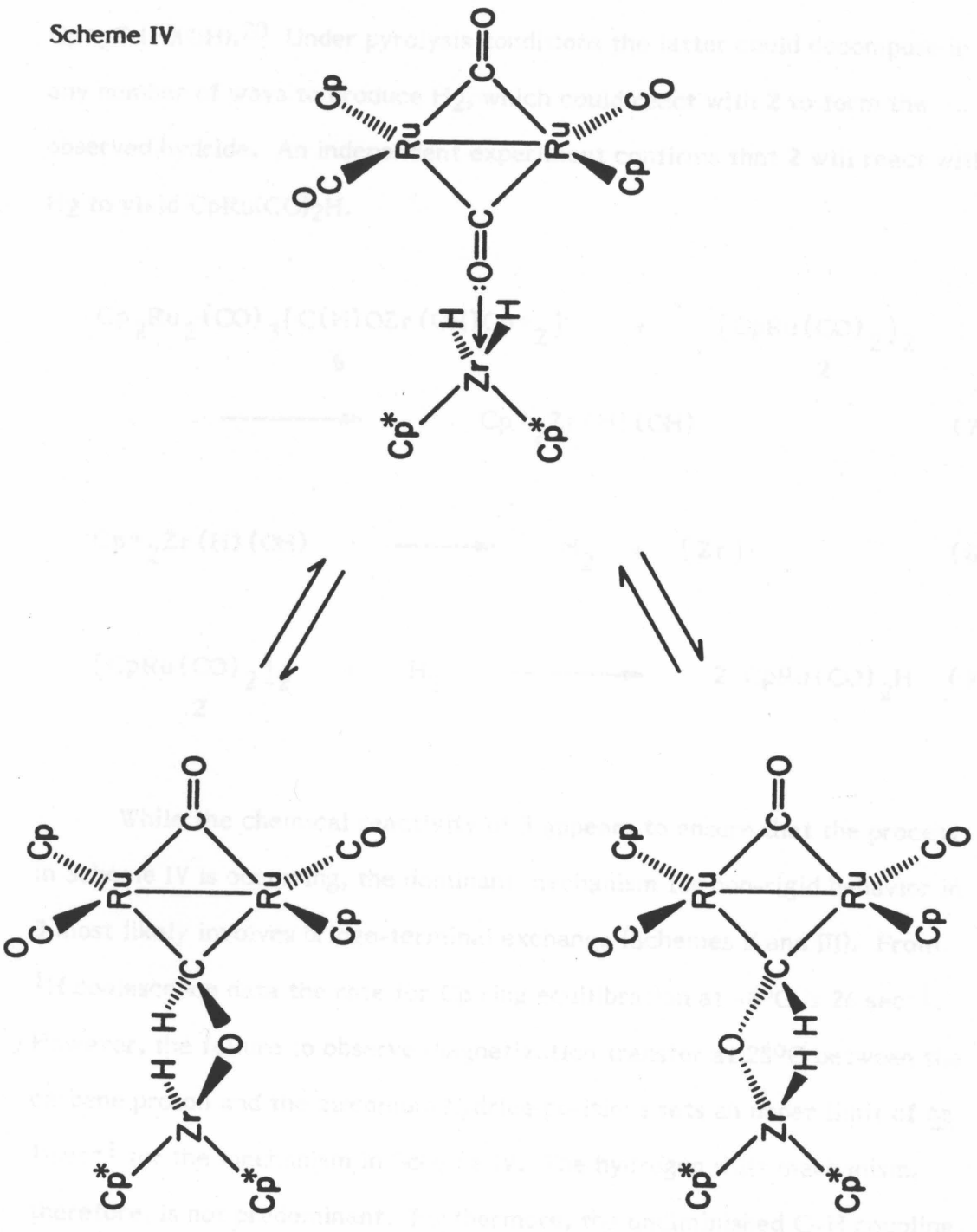
intermediate. Transfer of the other hydride to the carbonyl yields the carbene in which the environments of the Cp rings have been exchanged. Alternatively, the hydrogen shift might produce free **1** and **2** which then recombine with the same net randomization of Cp rings. The reaction chemistry of **3** provides ample evidence for the reversibility of the addition of hydride across the carbonyl C-O bond. For example, reaction of **3** with CO to form **2** and $Cp^*_2Zr(CO)_2$ is most easily explained by the presence of a small equilibrium concentration of **1** which under CO reductively eliminates H_2 and forms the carbonyl complex.[18] Wolczanski reported a similar transformation of a tungsten zirconoxy carbene, albeit under considerably more forcing conditions.[3]

Deuterium exchange with the hydride positions in **1** has been shown to be remarkably facile even at -80°C.[19] While exchange with the mono-hydride in **3** would not be unprecedented, deuteration of the carbene position reasonably requires some sort of hydride-carbene interchange.

Similarly, reaction of the iodide and trifluoroacetate derivatives of **3** with MeI and CF_3COOH to form **2** and $Cp^*_2ZrI_2$ and $Cp^*_2Zr(OOCCF_3)_2$ most likely proceeds through intermediate Cp^*_2ZrHX (X = I, CF_3COO) generated by a hydrogen shift from carbon to zirconium. The faster rate of reaction for addition of a second equivalent of CF_3COOH implies that production of Cp^*_2ZrHX (X = CF_3COO) is considerably faster than when X is OH or I. This might be due to destabilization of the trifluoroacetate derivative of **3** by the steric bulk of the acetate group.

The decomposition of **6** to **2** and $CpRu(CO)_2H$ is another case in point. A hydrogen shift from the carbene back to the zirconium would produce **2** and

Scheme IV



$Cp^*_2Zr(H)(OH)$.[20] Under pyrolysis conditions the latter could decompose in any number of ways to produce H_2, which could react with **2** to form the observed hydride. An independent experiment confirms that **2** will react with H_2 to yield $CpRu(CO)_2H$.

$$\underset{\mathbf{6}}{Cp_2Ru_2(CO)_3(C(H)OZr(OH)Cp^*_2)} + \underset{\mathbf{2}}{(CpRu(CO)_2)_2} \longrightarrow + \; Cp^*_2Zr(H)(OH) \qquad (7)$$

$$Cp^*_2Zr(H)(OH) \longrightarrow H_2 + (Zr) \qquad (8)$$

$$\underset{\mathbf{2}}{(CpRu(CO)_2)_2} + H_2 \longrightarrow 2\; CpRu(CO)_2H \qquad (9)$$

While the chemical reactivity of **3** appears to ensure that the process in Scheme IV is occurring, the dominant mechanism for non-rigid behavior in **3** most likely involves bridge-terminal exchange (Schemes II and III). From ^1H coalescence data the rate for Cp ring equilibration at -4°C is 26 sec^{-1}. However, the failure to observe magnetization transfer at 28°C between the carbene proton and the zirconium hydride positions sets an upper limit of ca. 1 sec^{-1} for the mechanism in Scheme IV. The hydrogen shift mechanism, therefore, is not predominant. Furthermore, the undiminished C-H coupling constant of the carbene carbon at high temperatures is consistent with this proposal. It is not possible, however, to distinguish between the mechanisms in Schemes II and III on the basis of these data.

Reaction of 3 with Lewis Acids. While protonation with an acid such as water or CF_3COOH with **3** results in reaction at the hydride position and formation of hydrogen and substituted **3**, stronger acids attack the oxygen of the zirconoxy carbene. This is similar to the action of Lewis acids on the iron carbene $Cp_2Fe_2(CO)_3(C(H)(OCH_3))$ which yield $(Cp_2Fe_2(CO)_3(CH))^+$ (eq. 10).[8b] Both Casey and Pettit have shown that this bridging methylidyne

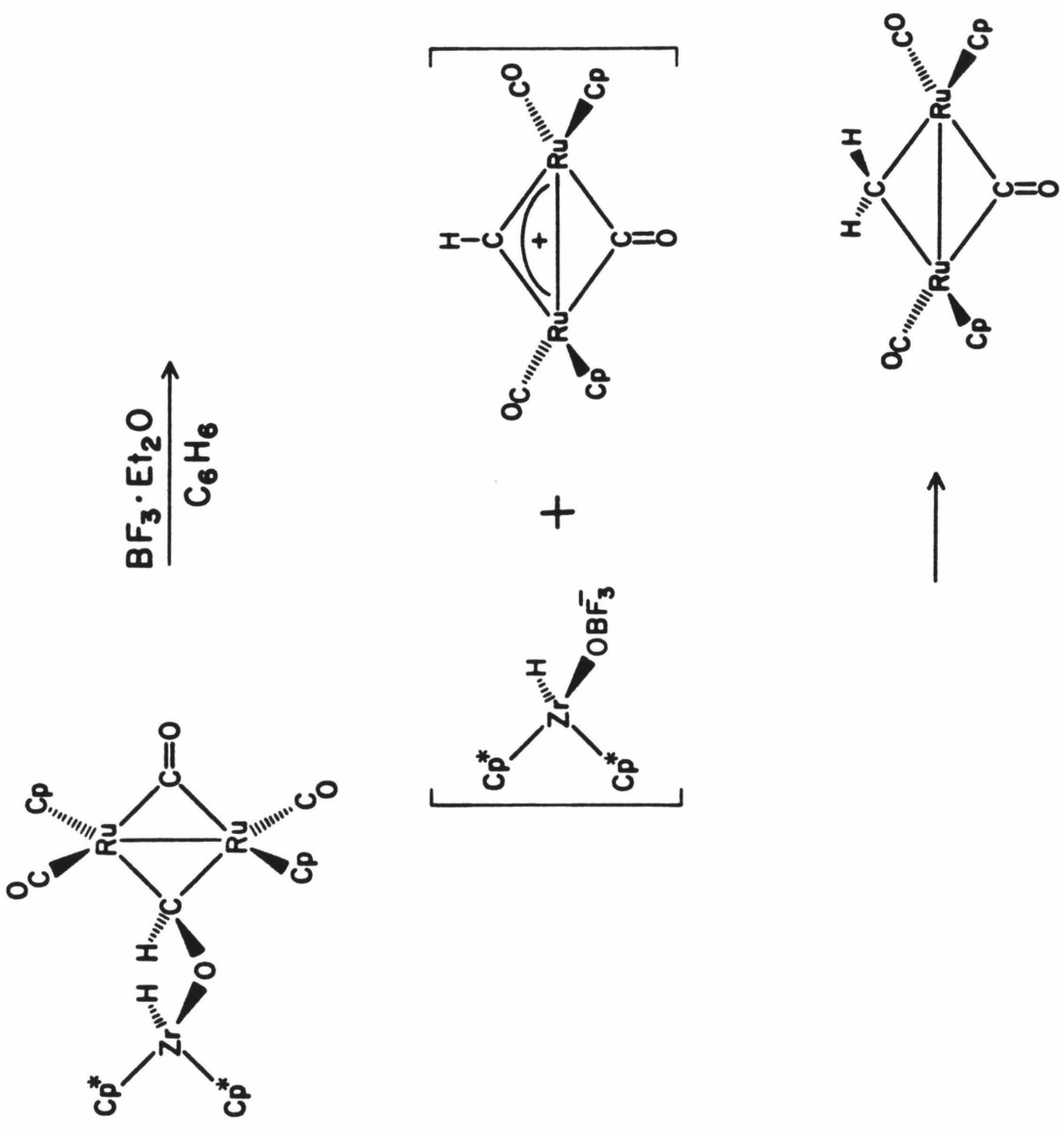
$$Cp_2Fe(CO)_3(C(H)(OCH_3)) \xrightarrow{Ph_3C^+ \text{ or } H^+} (Cp_2Fe_2(CO)_3(CH))^+ \qquad (10)$$

$$(Cp_2Fe_2(CO)_3(CH))^+ \xrightarrow{H^-} Cp_2Fe_2(CO)_3(CH_2) \qquad (11)$$

is attacked by hydrides to produce $Cp_2Fe_2(CO)_3(CH_2)$ (eq. 11).[8] The presence of an internal hydride source in **3** suggests that a reaction sequence similar to equations 10 and 11 occurs in the reaction of **3** with $HBF_4 \cdot Me_2O$ or $BF_3 \cdot Et_2O$ (Scheme V). The formation of $\underline{d}_2$-**7** from $HBF_4 \cdot Me_2O$ and $\underline{d}_2$-**3** confirms that the second methylene proton is transferred from the zirconium.

$$\underset{\underline{d}_2\text{-}\mathbf{3}}{Cp_2Ru_2(CO)_3(C(D)OZrDCp^*_2)} + HBF_4 \cdot Me_2O \longrightarrow \underset{\underline{d}_2\text{-}\mathbf{7}}{Cp_2Ru_2(CO)_3(CD_2)} + \ldots \qquad (12)$$

Scheme V



The synthesis of **7** directly from **2** is an attractive alternative to the published procedure, which requires two steps with a 35% overall yield.[21] Use of **1** as a reducing agent is not practical, of course, so the commercially available $LiBEt_3H$, **8**, was tried. Gladysz reported several treating metal carbonyl dimers including $(CpFe(CO)_2)_2$ with **8** in a general procedure for preparing lithium salts of the metal anions.[22] He noted, however, that while THF was a suitable solvent for most dimers, a more polar mixture such as 50% THF/HMPA was required to cleanly reduce $(CpFe(CO)_2)_2$ to $Li(CpFe(CO)_2)$. Several groups have reported reduction of terminal carbonyls to formyl, hydroxymethyl, and methyl groups, with non-polar solvents resulting in the most reduced products.[23-25] The present studies show that while **7** can be synthesized in 60% isolated yield from **2** and **8** in toluene, no **7** is produced when the reaction is run in THF. Clearly the greater Lewis acidity of BEt_3 in non-coordinating solvents is important in the C-O scission step in the reduction of carbonyl ligands.

Experimental Section

General Considerations. All manipulations were performed using either glove box or high vacuum line techniques. Hydrocarbon solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[26] NMR solvents, toluene-$\underline{d}_8$ and benzene-$\underline{d}_6$ were also purified by transfer from "titanocene". Hydrogen was passed through MnO on vermiculite and then over 4 Å molecular sieves.[27] Carbon monoxide (MCB) was used directly from the cylinder. $Cp^*_2ZrH_2$,[28] $Cp^*_2HfH_2$,[29] Cp^*_2ZrHCl,[5] $(CpRu(CO)_2)_2$[30,31] and $Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2$[1a] were synthesized as described previously.

Infrared spectra were measured on a Beckman 4240 spectrophotometer. ^1H NMR spectra were obtained using Varian EM-390 and JEOL FX-90Q spectrometers. ^{13}C NMR spectra were obtained using the JEOL FX-90Q instrument. Samples for ^{13}C NMR experiments were generally prepared with ^{13}CO enriched $(CpRu(CO)_2)_2$[12] and ca. 0.1 M added $Cr(acac)_3$[32] to facilitate observation of the carbonyl carbons. Coupling constants were measured from either gated spectra or spectra obtained using the INEPT pulse sequence. The magnetization transfer experiments were run as described elsewhere.[33] Elemental analyses were performed by Bernhardt Microanalytical Laboratory, Dornis and Kolbe Microanalytical Laboratory or Larry Henling at the CIT Analytical service.

$Cp_2Ru_2(CO)_3(C(H)OZrHCp^*_2)$, 3. a) From 1 and 2. A solution of 1 (330 mg,0.909 mmol) and 2 (300 mg, 0.676 mmol) in 30 mL toluene was stirred for 30 min at -80°C, warmed to 25°C and stirred for an additional 1 h. After filtration the solvent volume was reduced to 5 mL and 5 mL petroleum ether added. Stirring for 30 min produced a bright yellow slurry, which upon

filtration yielded 393 mg (73%) of yellow solid.

Anal. calcd. for $C_{34}H_{42}O_4Ru_2Zr$: C, 50.54; H, 5.24; Ru, 25.02; Zr, 11.28. Found: C, 51.21; H, 5.40; Ru, 24.39; Zr, 10.93.

b) From $Cp^*_2Zr(O_2C_2)Cp_2Ru_2(CO)_2$ and H_2. A slurry of $Cp^*_2Zr(O_2C_2)$-$Cp_2Ru_2(CO)_2 \cdot 0.5\ C_7H_8$ (500 mg, 0.587 mmol) and 20 mL petroleum ether was stirred under 1 atm H_2 for 14 h at 25°C. Filtration yielded 393 mg (83%) of yellow solid. Compound **3**-d_2 was prepared by method (b) using D_2.

$Cp_2Ru_2(CO)_3$ [C(H)OHfHCp*$_2$), **4**, was prepared by method (a) using $Cp^*_2HfH_2$.

Anal. calcd. for $C_{34}H_{42}HfO_4Ru_2$: C, 45.61; H, 4.73. Found: C, 45.85; H, 4.75.

Reaction of 3 Under CO. Compound **3** (10 mg, 0.012 mmol) and benzene-d_6 (0.3 mL) were added to an NMR tube, CO (0.33 mmol) was introduced at -196°C and the tube sealed. After 14 h the ^1H NMR spectrum showed complete conversion to **2** and $Cp^*_2Zr(CO)_2$.

Reaction of 3 with CH_3I. Compound **3** (15 mg, 0.019 mmol) and benzene-d_6 (0.3 mL) were added to an NMR tube into which was distilled CH_3I (0.036 mmol) at -196°C. The tube was sealed and the course of the reaction monitored by ^1H NMR. After 20 min at 25°C conversion of **3** to a new compound with resonances at δ 5.12 (s, 10H, Cp), 2.00 (s, 30H, Cp*) and 12.80 (s, 1H, CH) was ca. 70% complete. A small quantity of **2** was also observed. After 15 h no **3** remained, and conversion to **2** was about 60% complete. $Cp^*_2ZrI_2$ and CH_4 were also observed.

Reaction of 3 with CF_3COOH. Compound **3** (17 mg, 0.020 mmol) and benzene-d_6 (0.3 mL) were added to an NMR tube and sealed with a latex

septum. CF_3COOH (1 μL, 0.013 mmol) was injected *via* syringe. A ^1H NMR spectrum measured after *ca.* 30 sec showed **2**, **3** and a new product (δ 5.10 (s, Cp), 2.78 (s, Cp*)) in a ratio of *ca.* 2:6:3. After addition of a second 1 μL aliquot of CF_3COOH, the ratio was 6:2:5. A third aliquot was added, and after 15 min only **2** and $Cp^*_2Zr(OOCCF_3)_2$ were observed.

Reaction of 3 with $BF_3 \cdot Me_2O$. Compound **3** (15 mg, 0.019 mmol) and benzene-d_6 were added to an NMR tube and sealed with a latex septum. $BF_3 \cdot Me_2O$ (2 μL, 0.011 mmol) was injected *via* syringe. The resulting brown solid was centrifuged to the top of the tube. A ^1H NMR spectrum showed a single Cp* resonance at δ 1.87 and signals for a mixture of *cis* and *trans* isomers of $Cp_2Ru_2(CO)_3(CH_2)$ (70% conversion based on integrated intensities relative to internal TMS).

Reaction of 3 with $HBF_4 \cdot Et_2O$. Treatment of 3 (15 mg, 0.019 mmol) with $HBF_4 \cdot Et_2O$ (4 μL, 0.030 mmol) as above resulted in 54% conversion to $Cp_2Ru_2(CO)_3(CH_2)$. As with $BF_3 \cdot Me_2O$, the only CpRu containing species remaining in solution besides $Cp_2Ru_2(CO)_3(CH_2)$ was a small amount of **2**.

Synthesis of $Cp_2Ru_2(CO)_3(CH_2)$ from 2. Compound **8** (2.5 mL, 1 M in THF) was added to a solution of **2** (505 mg, 1.14 mmol) in 30 mL toluene and the reaction mixture was stirred for 2 h at 25°C. Solvent was removed to yield a dark oil which contained **2** and **7** in a 1:2 ratio (^1H NMR). The oil was dissolved in 30 mL toluene and an additional 1 mL **8** added. After 2 h at 25° the reaction mixture was opened to the air and poured into 50 mL H_2O. The organic phase was separated and washed twice with H_2O, dried over $MgSO_4$ and column chromatographed (SiO_2/C_6H_6). A single yellow band was

collected and the solvent flash evaporated. Recrystallization from toluene/petroleum ether yielded 280 mg (57%) of yellow crystals, pure by ^1H NMR analysis.

$Cp_2Ru_2(CO)_2[C(H)OZrHCp^*_2]_2$. A mixture of **3** (111 mg, 0.14 mmol) and **1** (55 mg, 0.15 mmol) in 10 mL toluene was stirred for 2 h at 25°C. The resulting mixture was filtered and dried to yield 134 mg (82%) of the yellow solid.

Anal. calcd. for $C_{54}H_{74}O_4Ru_2Zr_2$: C, 55.35; H, 6.37. Found: C, 55.71; H, 6.31.

$Cp_2Ru_2(CO)_3[C(H)OZr(OH)Cp^*_2]$, 6. Into a solution of **3** (142 mg, 0.176 mmol) in benzene (25 mL) was injected H_2O (3.5 μL, 0.194 mmol) at 25°C. The yellow solution was stirred for 4 h, filtered, then the solvent volume reduced to 5 mL. Petroleum ether (10 mL) was added and the slurry was stirred an additional 45 min followed by filtration to yield 100 mg (70%) of yellow solid.

Anal. calcd. for $C_{34}H_{42}O_5Ru_2Zr$: C, 49.55; H, 5.14. Found: C, 49.43; H, 5.15.

Reaction of 2 with Cp^*_2ZrHCl. Compound **2** (24 mg,0.054 mmol) Cp^*_2ZrHCl (24 mg, 0.063 mmol) and toluene-d_8 (0.3 mL) were sealed in an NMR tube. The course of the reaction was monitored over three days, at which time formation of **5** was complete.

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